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On the Origin of the Movements of Camphor on Water and Other Allied Phenomena.

BY

L. A. Ramdas, M.A.,

Palit Research Scholar, University of Calcutta.

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3. Movements of Soluble Solids.
4. Movements of Dye-Stuffs.
5. Formation and Disappearance of Surface Films.
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7. Theory of the Movements.
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(*Plates I, II, III*).

1. *Introduction.**

It is a well-known fact that particles of camphor, when thrown on a clean surface of water, begin to move about in a very lively manner. That very similar movements accompanied by violent deformations are shown by lenses of semi-oily liquids like ortho-toluidine and xylidine has been noted by C. R. Darling.[1] More recently Geppert[2] has described the rotational movements of some aniline dye-stuffs and he explains these movements as recoil-effects against the thin films that are sent out by the crystals over the surface of water. Volmer and Mahnert,[3] from their study of the spreading of Benzo-phenon on a clean surface of mercury, and Marcelin,[4] from his experiments with camphor on water, have established that, in the cases they deal with, the spreading occurs as a mono-molecular film. The former authors find that the process of *surface* solution of Benzo-phenon on mercury is 10,800 times as quick as the evaporation from the crystal itself.

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* All references are given at the end of the paper.

It is clear from the previous studies cited above that the movements are shown by a very large number of organic compounds, both solid and liquid, and that they are intimately related to the spreading of these substances on the surface of water.

From the recent researches of Rayleigh,[5] Miss Pockels,[6] Hardy,[7] Langmuir,[8] N. K. Adam[9] and others,[10] many interesting facts regarding the structure of mono-molecular films of insoluble organic compounds like the fatty acids have emerged. The most notable of these is that the films can remain under suitable conditions in three states corresponding to those of matter in bulk, *viz.*, solid, liquid, and gaseous. In fact Cary,[11] Schoefield, Rideal and Adam[12] have shown that the film in the gaseous state obeys a law connecting the area and the surface pressure of the molecules in the film which is essentially of the same form as $p\,v = R\,T$ for gases. It is not difficult to understand then that when, on the surface of clean water, a foreign substance is placed, the surface pressure would tend to equalise and so the substance would spread over the whole area with quite an appreciable velocity in a way analogous to the expansion of a gas into a vacuum. The actual velocity of the spreading and the state of the film depend on the temperature and the strength of the lateral attraction of the molecules for one another. If the substance is insoluble, a state of equilibrium is very quickly attained as in the case of oleic or palmitic acid. When the substance is soluble or volatile like amyl alcohol or camphor, the spreading is continuously maintained over a definite area depending on the solubility, until either the supply is exhausted or the water below has got quite saturated with the substance. Until this state is reached the movements go on vigorously.

There are at present two alternative theories for these movements. One of them supposes that the movements are mere recoil effects and the other that they are due to differences in the rate of solution of the substance over the boundary and the consequent difference in the surface tension forces acting on the body. In the course of the present paper, it will be clear that recoil cannot explain the movements in those cases where the films are mono-molecular as neither the mass of the films spreading nor their velocity of spreading is sufficiently large to account for the vigorous movements of the big particles from which they spread. The second theory does not appear to be in agreement with the facts. As a result of the present investigation a new theory, which may be called the *stream-line theory* has been put forward. Here the surface tension differences are related to the form of the lines of flow of the material from the edges of the substances. In those regions surrounding the substance where the lines of flow converge together, there is a considerable diminution of surface-tension and in those regions where they diverge the surface tension is diminished in a smaller degree.

It will be shown that recoil-effects come in only when the spreading is not mono-molecular and the material is shot off from the source in particles of considerable size or when the spreading becomes suddenly unidirectional from a localised point on the edge of a lens floating on water. The conditions under which the movements occur and the actual nature of the films that spread have been studied in the case of a large number of liquids and solids. The surface tension effects of spreading films have been measured by a new method and the structure of the films themselves studied optically.

2. *The Movements of Liquid Lenses on the Surface of Wāter.*

When a small quantity of amyl alcohol is poured on the surface of water, it splits into a number of lenses from which very violent solution takes place for a few seconds. This initial and rapid solution having abated, the lenses that are left behind get deformed and move about with great agility. A lens gets deformed slightly into concave on one side and then further deformed in the same direction at an accelerated rate, while the lens as a whole moves away abruptly as if it is being pushed violently from the deformed side. Once the concavity begins to form, the deformation is suddenly accelerated and the movement of the lens is in every case away from the deformed side. The deformation is often sufficiently violent to split the lens into two or to give it the most fantastic shapes. These feats of distortion are most amazing and, when projected on a screen, appear very life-like and spectacular. The bigger lenses are most easily affected, the smaller ones sometimes partaking of their movements though often enough moving spontaneously as a result of similar forces acting at their own boundaries. The smaller lenses are naturally given translational movements while the bigger ones are more easily deformed.

Of the liquids which show these movements, the higher alcohols like amyl and octyl alcohols are most conspicuous. Many other liquids like orthotoluidine, xylidine, chlorobenzene and bromo-benzene behave in a similar way. With amyl alcohol the movements are seen at their best and are reproducible without any trouble. In the case of octyl alcohol, in addition to occasional movements, the lenses, when their number is not very large, often stand still at intervals and perform star-shaped oscillations of large frequency.

The author has succeeded in taking good cinematographic pictures of the movements of amyl alcohol lenses. The movements were projected by means of a vertical projection apparatus provided with a reflecting prism to throw the image on a vertical screen. The glass vessel containing the water and the floating lenses had a plane bottom and did not distort the image in any way. Sun-light was used as very strong illumination was essential. The movements on the screen were then photographed with a cinematograph camera fitted with a Zeiss (F-3·5) lens. Two hundred feet on the standard negative film were exposed. Some very striking sections are reproduced in Plate I (Figures *a*, *b*, *c* and *d*) where the successive deformations and the progress of the movements are clearly recorded.

The rapidity of the movements depends on the rate of removal of the films spreading from the lenses either by solution or evaporation. The influence of solution and evaporation is shown by the following experiment.

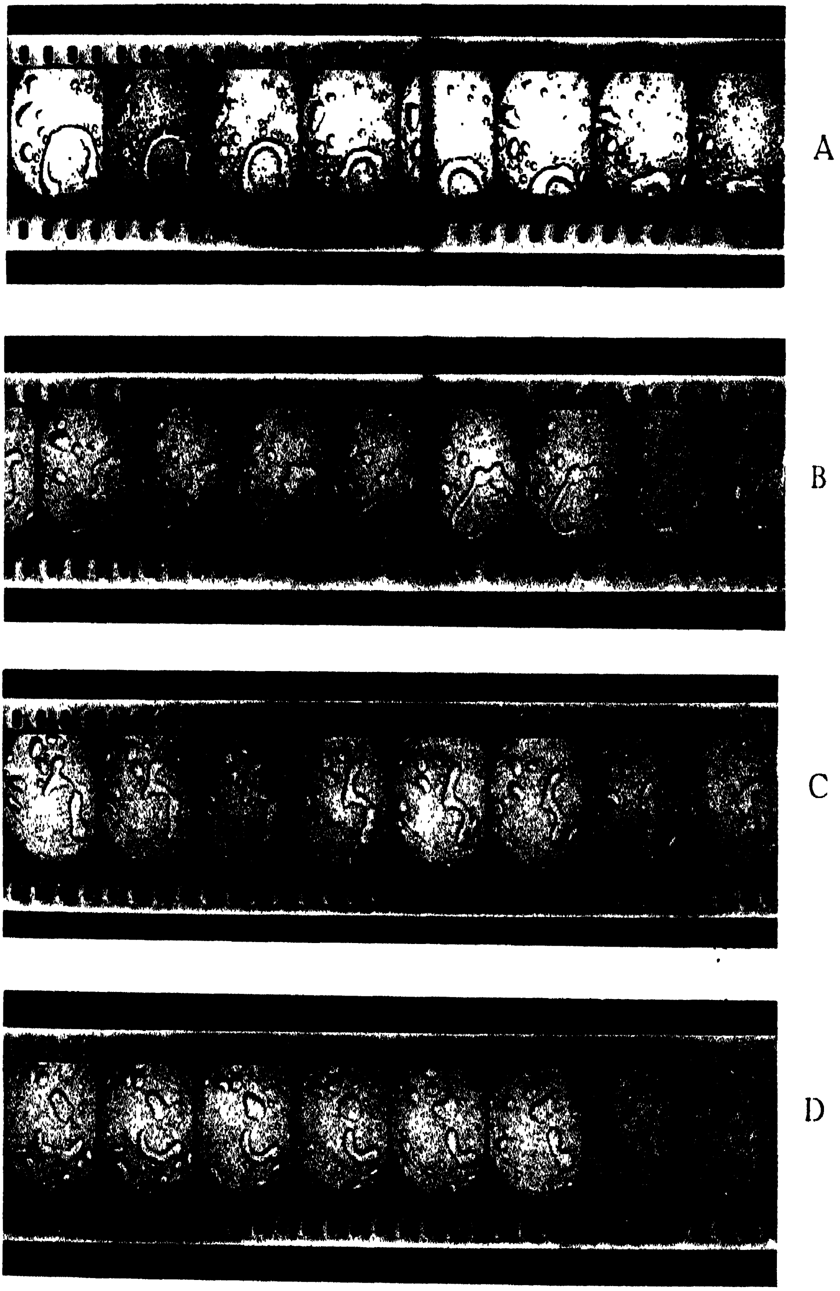
A glass vessel was filled with water nearly up to the brim and sufficient amyl alcohol poured on the surface. The vessel was then nicely covered with a clean glass plate. This prevented evaporation from taking place soon after the intervening space had got saturated with alcohol vapour. In spite of this the movements were not retarded in any way as solution could take place. It required about forty minutes to completely stop the movements, *i.e.*, to saturate the water below the surface. When this had happened, no more transfer of the alcohol from the surface was possible and the movements ceased slowly. When, however, the glass plate covering the vessel was removed, the lenses got lively again as evaporation could then proceed. As the water nearly filled the vessel, when the glass plate was once again replaced to cover it, the space between got saturated in a few seconds and the movements soon slowed down and stopped completely.

3. *Movements of Soluble Solids.*

When large particles of solid substances like camphor, antipyrin, resorcin, etc. (see Table II for a list of other substances) are thrown on a clean surface of water, they begin to move about very vigorously. To observe these movements very successfully the glass vessel has to be cleaned thoroughly with soap and rinsed several times with water. For cleaning the surface of the water after filling a vessel, the top layer is suddenly blown off. The fresh surfaces thus obtained are quite satisfactory. One is quite familiar with camphor movements. These last for a long time until the water below gets saturated with camphor. Owing to evaporation the movements do not cease completely, but with most of the solid substances solubility plays a more important part than with the more volatile substances. In the case of antipyrin, resorcin, etc., the movements do not last for a long time, as these substances are more soluble than camphor. When the crystals are, as is often the case, needle-shaped, the abruptness as well as the swiftness of the movements are very remarkable. If the crystal has perfectly plane boundaries there is no movement for an instant, but when the slightest irregularity develops owing to the rapid *surface solution*, the crystal abruptly moves away in the opposite direction with such violence that even the water surface in its wake is visibly depressed. In a few seconds the whole crystal has disappeared completely by solution.

In the previous paragraphs only the movements of substances which are to a more or less extent soluble or volatile have been dealt with. It is very interesting to find that similar movements can be obtained even in the case of a substance which is neither soluble nor volatile in the usual sense, but has *superficial or surface solubility*, *i.e.*, which merely spreads on clean water as a mono-molecular film. This has been done by using paper strips coated with oleic acid.

In this case the spreading of the oleic acid when the paper strip is placed on the clean surface of water lasts only for a fraction of a second, *i.e.*, the time taken for the whole



Amyl alcohol drops on water.

surface to be covered with a mono-molecular film of the oleic acid. If the shape of the paper strip is perfectly circular no movement takes place. When, however, a V is cut on one side of the circular paper strip, a very violent movement of the paper strip away from the V is observed. If instead of the V, a concave cut is made on one side, a similar movement away from the concavity takes place. In the case of a semicircular strip, the movement is away from the straight edge.

When the paper strips are coated with amyl alcohol or some other liquid which is soluble in water, these movements persist for a long time until all the substance has been removed by spreading and subsequent solution of the spread film.

Similar movements away from the concave edges can be observed with camphor blocks cut into the required shapes. A perfectly circular block of camphor is not so easy to prepare, but the nearer the shape approximated to a circle, the less liable was it to be moved about.

The experiments with differently shaped paper strips coated with amyl alcohol and camphor blocks cut into various shapes are repeated by keeping these sources fixed and dusting the surface of the water. The actual distribution of the *stream lines* and its dependence on the shape of the source are then clearly brought out. In front of every concavity at the edge very powerful streaming, focussed at a distance from the edge, may be observed. If the edge is straight at other parts, the streaming is less powerful and not clearly focussed. The boundary of the cleared area approaches nearest the sharp corners and projections. To observe these effects clearly it is just as well that the water surface has some slight initial contamination on the surface, as otherwise the whole area may be swept out clean by the advancing film. The accompanying figure gives a vivid picture of the distribution of the stream lines (see Fig. 1). A is the piece of camphor having the shape of the crescent moon with a concavity on one side and a convexity on the opposite side. The dotted line shows the actual extent of the spreading and the thick lines leaving the edges show the path and distribution of the stream-lines.

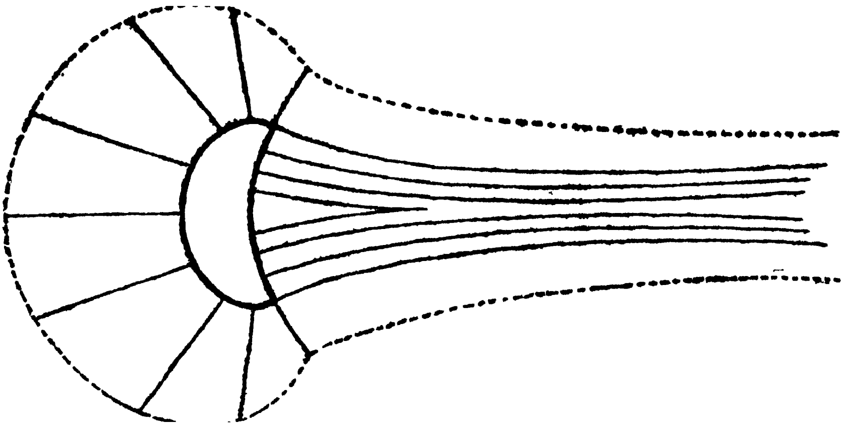


Fig. 1.

A square piece of camphor having a concavity on each side situated near the two opposite corners begins to show rapid rotational movement when left free on a clean surface of water. This is evidently due to the forces acting at the corners forming a couple, whose strength depends only on the purity of the water surface and the dimensions of the piece. It is easy to see that the very vigorous rotational mevements usually observed with the smaller particles arise in a similar manner.

These experiments with paper strips and camphor blocks are extremely helpful in understanding the forces which give rise to the movements of the substances floating on water.

4. *Movements of Dye-Stuffs.*

When we come to the dye-stuffs like methyl violet, tetriod-fluorescein, eosin, etc., the phenomena that cause the movements as well as the movements themselves are much easier to see. Most of them are not very soluble in bulk, but their *superficial or surface solution*, while it lasts, is a very striking phenomenon.

The methyl violet and tetriod-fluorescein were presented to Prof. Raman by Prof. Frumkin (Moscow, Karpow-Institute fur Chemie) who was working on the electrical properties of films of these substances on water. They were very pure and proved very useful in the present investigation.

Methyl Violet.

If a small crystal is left free to move about on a clean surface of water, initially it often happens that the crystal stands still while the spreading of the substance takes place rapidly and uniformly. The crystal is surrounded by a clear transparent area which again is surrounded by a coloured film of the substance extending up to the walls of the vessel and slowly getting more and more coloured owing to the accumulation of the substance shot across the clear area by the crystal. This steady state lasts only for a few seconds and the crystal begins to shoot off thick coloured streams of the dye-stuff from one, two or three points on its line of contact with water in the form of streaks and moves away very rapidly from these directions of extra ejection of material. Very often the movements become gradually closing spirals as the already spread film surrounding the crystal resists linear motion over a large distance. These spiralling movements are extraordinarily beautiful to behold especially when projected on a screen. Some good photographs of the spiral movements are reproduced in Plate II, Figures 1, 2, 3 and 4. The vigour of the spiralling depends only upon the amount of material already spread. When the spiralling finally ceases, the ejection of the streaks is curbed for a time, but does not completely stop. Instead of the continuous streaming we get spasmodic and periodic shooting out of the material which shows up like a train of coloured wave-lets. Finally even this stops and the crystal goes down into the water abruptly.

When a small crystal attached to the tip of a clean platinum wire is placed on a thoroughly cleansed surface of water, one can observe a rapid spreading of the material. The crystal is seen to be surrounded, as mentioned before, by a clear transparent circular area which again is surrounded by the coloured film. The clear area is a region of rapid spreading which slowly contracts owing to the tendency of the film surrounding it to expand into it. The rapidity of the spreading may be observed by throwing some tiny pieces of paper on the surface near the crystal when they are shot across the clear area rapidly and later sail out less quickly across the coloured region. The spreading of the dye-stuff continues until the clear space slowly contracts owing to the compressing force exerted by the film outside. The spreading then takes place from particular points in the form of narrow, richly coloured streaks and finally these streaks cease to be continuous. Small fragments are ejected periodically whenever the streaming matter is able to break through the resisting coloured film. Finally everything ceases and the crystal if shaken loose from the platinum loop, promptly goes down into the water below.

An attempt was made to find out the nature of the clear space surrounding the methyl violet. A strong beam of sun-light was focussed on the clear space when the focal spot appeared, contrary to expectation, as a strongly yellowish-orange spot. This is of the same colour as that shown by a dry crystal by reflected light. This suggested that the transparency of the clear space is not merely due to the thinness of the rapidly spreading film but to the absence of any dissolved material and that the material may be shot across the clear space as microscopic crystals ! This is found to be actually the case. When the focal spot is viewed through a microscope, fine and well defined

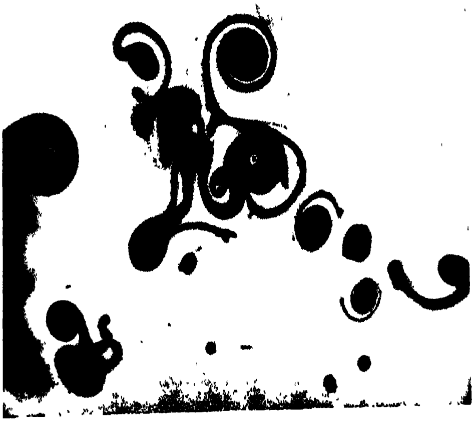


Fig: 1.

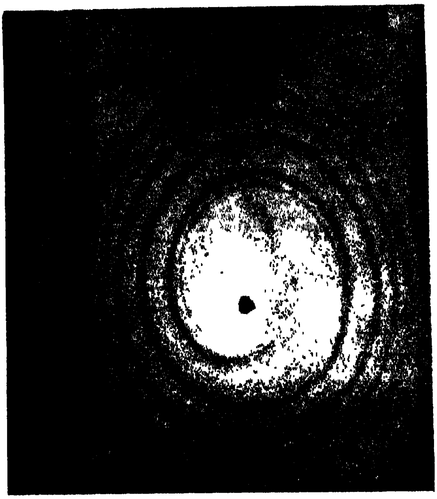
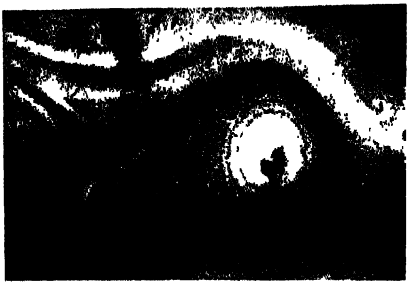


Fig: 2



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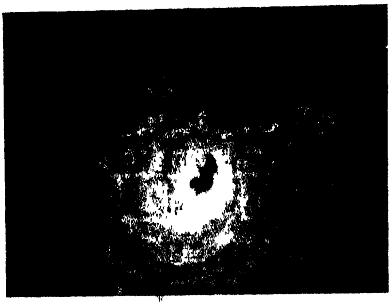


Fig: 4.

Movements of dye-stuffs on water.

micro-crystals are found leaving the big crystal at a very rapid rate. The streaming is not equally intense from different parts of the crystal. It may be possible that the crystals leaving the bigger one are *cleaved off* by the attractive forces of the water molecules at the surface in its neighbourhood from planes of weaker binding. These micro-crystals later dissolve on the water surface slowly, giving rise to the coloured film outside. It was found that even after the spreading had completely stopped and the crystal itself had sunk into the water, the whole surface was covered with a very large number of undissolved crystals. The quantity of the dissolved dye-stuff in excess of that required to saturate the surface went into the water very promptly. The liner coloured streaks which were ejected during the later stages were also composed of these micro-crystals.

If the surface is now touched by a greased platinum tip, the whole film is swept out and pushed down into the water below like a curtain. This shows that the film is not rigid like some solid films which will be described later on.

If on a surface of water saturated with a methyl violet film a few camphor particles are thrown, they begin to move about very quickly, showing that the surface tension has not been lowered below the camphor point. The spreading films of camphor produce clear areas round the particles driving away the film of dye-stuff. If now a few more crystals of methyl violet are thrown on the water surface, they shoot into the clear areas of the camphor particles and often attach themselves to the camphor particles and revolve merrily with them while allowing the dye-stuff films to spread into the clear areas surrounding them. The film of the dye-stuff on other parts of the surface goes down now and then owing to the agitation and renewed spreading. These methyl-violet-camphor pairs continue as long as the methyl violet lasts and then the camphor particles are left alone to continue their movements.

Tetriod-fluorescein, Eosin and Erythrosin.

These dye-stuffs are available in the form of powders. When small quantities are thrown on a scrupulously clean water surface, quick spreading into films occurs. The films formed are solid films. This may be verified by touching the film after formation with a platinum wire having a minute trace of oil, when the film cracks in three or four directions. A picture of the cracked film is given in Plate III, Figure 4.

The film being solid, the movements of small lumps of the powder similar to those in the case of methyl violet take place on a comparatively feebler scale and last only during the short time taken for the whole surface to be covered with the solid film. Once this has taken place the movements completely cease and any excess of the material immediately goes down in the form of fine streaks. Camphor particles are quite dead when thrown on the surface, showing that they have no access to the water surface.

If instead of camphor a very small crystal of methyl violet is placed on the solid film, it immediately bursts the film and clears out a star-shaped space covered with the pinkish methyl violet film. The contrast between the orange solid film and the pink liquid film inside is an extremely beautiful sight. In the cleared area, the methyl violet continues to spin. For the success of this experiment the water surface has to be extraordinarily clean.

Behaviour of the Dye-stuffs on an Oily Water Surface.

If the water surface is not clean but contaminated, the dye-stuffs behave quite differently. The film of oil covering the surface prevents *surface solution* and the crystals at once go down into the water leaving beautiful coloured trails behind them. These trails suggest a close resemblance to the inter-traction phenomena discussed recently by N. K. Adam and G. Jessop.[13] The trails have very well-defined boundaries and diffuse extremely slowly into the surrounding

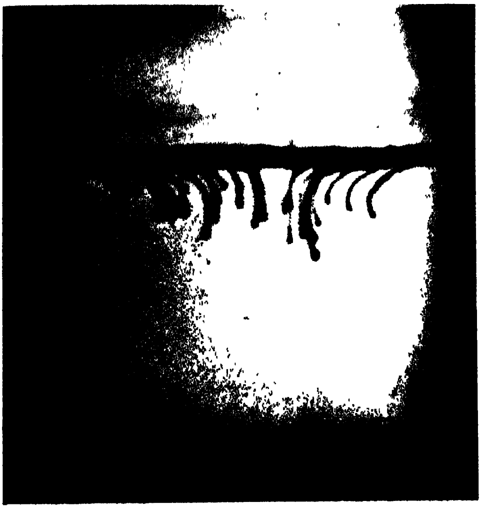


Fig. 1.

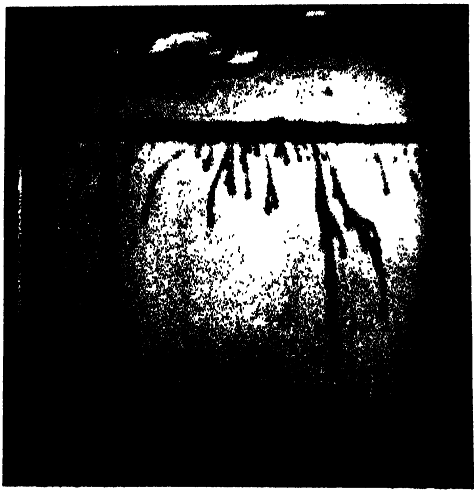
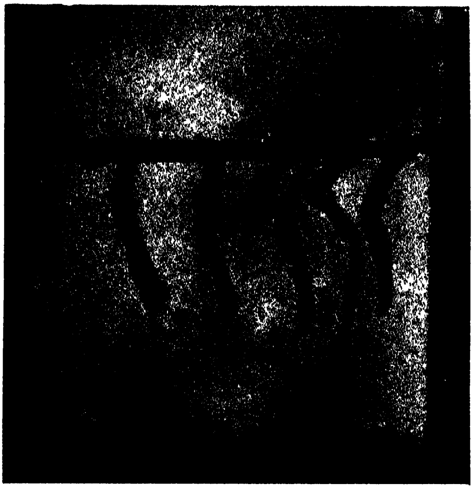


Fig: 2.



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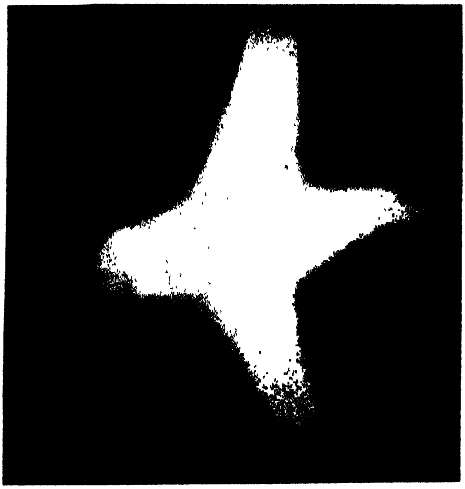

Fig: 4.

Behavior of dye-stuffs on water.

water. When illuminated by a beam of sun-light they show beautiful fluorescent colours and, when projected on a screen, the actual going down of the trails is a striking phenomenon. The methyl violet shows this less conspicuously than the other dye-stuffs. The same phenomenon may be reproduced if, instead of oil, the surface is saturated with the corresponding dye-stuff. Figures 1, 2, and 3, Plate III, illustrate these effects.

The movements above described are also shown by a very large number of substances which are given in Table II.

5. *Formation and Disappearance of Surface Films.*

Without complicating matters by using large quantities of these substances, it is very instructive, first of all, to study the spreading of mono-molecular or extremely thin films on a fresh surface of water. The physical properties of these films whether transient as in the case of soluble or volatile substances, or permanent as in the case of the fatty acids, has also to be properly understood before one can attempt an explanation of the movements described. The spreading of traces of organic compounds, both liquid and solid, is described below.

(*a*) *Liquids.*—A clean surface of water contained in a glass vessel was obtained by blowing off the top layer and, after the agitation had subsided, the surface was dusted with fresh lycopodium powder. The surface was then touched at the centre by a platinum wire conveying a film of a liquid like methyl alcohol in a loop at its end. The liquid then spread quickly on the surface driving away the lycopodium and forming a clear circular area which was maintained as long as there was any liquid at the centre. The substance was spreading all the while, the spread substance disappearing by solution and evaporation at the outer regions of the cleared area. The area of the circle did not increase indefinitely as with a trace of oleic acid owing to the solubility of the liquid. When the supply of the substance was exhausted the spreading ceased and the clear area contracted rapidly and finally disappeared leaving the whole surface covered with the lycopodium. The quickness and area of the spreading depended on the substance used. An examination of a large number of liquids of reliable purity was possible as a supply of sixty organic compounds prepared by Kahlbaum was available. In the case of the alcohols, spreading over increasing areas took place as one ascended up the series starting with methyl and ending in octyl alcohol. With the propyl, amyl and octyl alcohols the spreading took place once, then the cleared circle closed up and often expanded slowly once again over a smaller area. This may be due to the heaping up of the substance at the centre by the closing up and the later spreading of this residual substance. In the case of the esters and the hydrocarbons of the pentane series similar spreading took place, but over smaller areas and without any secondary spreading. Benzene may not spread at all, if the liquid is perfectly free from dissolved oily matter, but with the sample used there was a very slight spreading into a circle of two or three millimetres in diameter. The substitution products however, which have active group or groups spread very quickly over several centimetres. Cyclo-hexane, as was expected from its benzene-like structure, did not spread at all. Toluene was found to be moderately active while its substitution products spread violently. An interesting result obtained by comparing the chlorides, bromides and iodides, was that the amount of spreading diminished in the order mentioned above.

It may be noted that non-polar substances like benzene, cyclo-hexane, carbon-tetra-chloride, carbon-disulphide, etc., do not spread (or only very little), while compounds having active groups like OH, COOH, NH_2, CHO, etc., are very active whether they are in the liquid or solid state. (See Table I for list of liquids that spread on water.)

In this connection attention may be drawn to the recent work of Burdon[14] on the spreading of one liquid on the surface of another. He describes experiments on the spreading of water and dilute solutions of acids and inorganic salts on a specially cleaned surface of mercury. The present author had been working an year ago on the scattering of light by a perfectly clean surface of mercury[15] obtained by repeated distillation in vacuo. An attempt was then made quite successfully to obtain this phenomenon with an ordinary surface of clean mercury in the open. This was done by using chemically purified mercury and obtaining the fresh surface by overflowing. A small drop of any alcohol was placed on the surface when the alcohol spread very quickly clearing out all the dust on the surface. As soon as this happened a part of the cleared area was isolated by placing a very clean glass ring on the surface. If a strong beam of sun-light was focussed on this area, after the alcohol had evaporated, the surface scattering by mercury was obtained. The intensity of scattering compared quite favourably with that in the case of the clean surface in vacuo.

Similar spreading on mercury was obtained in the case of the other alcohols, esters and fatty acids. If very large quantities were used the films were fairly thick, but if only traces were used the films were so thin that Newton's colours were not observed.

(*b*) *Soluble Solids.*—Returning to spreading on the surface of water, let us consider the behaviour of very small quantities of solid substances. Rapid spreading as a mono-molecular film takes place when a small piece of camphor attached to the loop of a platinum wire is held in contact with the clean surface of water previously dusted with lycopodium. The moment the camphor is removed, the clear circle rapidly contracts as a result of the solution of the camphor film. In a recent paper[16] Marcelin has the measured compressibiliiy of a camphor film and the rate of spreading of the film from a piece of camphor held in contact with water. From his velocity measurement and estimation of the quantity of camphor removed by spreading per hour, the area occupied by one camphor molecule in the spreading film comes out as $34{\cdot}56 \times 10^{-16}$ *sq. cm.*, which is of the same magnitude as the area occupied by a molecule in a stable but *expanded* film of palmitic acid. One may safely assume that the camphor film is mono-molecular. Similar spreading more or less violent than that of camphor is shown by a variety of other solid organic compounds (see Table II).

(*c*) *Dye-stuffs.*—The spreading of the dye-stuffs is somewhat different from those of the more or less soluble substances dealt with before. The films obtained are more permanent as the solubility is only slight. When very small particles of these substances are thrown on a very clean surface of water, they spread very rapidly into thin films which, except in the case of substances like methyl violet, are solid films and, when touched by a greased platinum point, crack in three or four directions. The edges of these cracks are very sharp and parts of the broken films may be moved about just like pieces of paper floating on water.

For dealing with the minutest trace of the substance an aqueous solution of tetriod-fluorescein was prepared in a clean vessel. When a drop of the solution was placed on a clean surface of water the film into which it spreads is not solid. The film contracts after a time and slowly gathers up into a solid film, but is initially a liquid film. To find out whether the film is mono-molecular, a dilute solution of definitely known concentration was prepared. Known quantities of the solution could be applied to the surface by taking a film of the solution on the loop of a clean platinum wire every time. The weight of the solution in the loop was previously found out so that from the area over which one film on the loop spread, the area per molecule in the film could be calculated.

The concentration of the prepared solution was $2{\cdot}2 \times 10^{-3}$ gr. per gramme of solution. The weight of the film on the loop was ·0014 gr. and it spread into a film of radius 1·3 cm. The molecular weight is 880, so that the area per molecule comes out as $24{\cdot}87 \times 10^{-16}$ sq. cm.

This value agrees with the area occupied by a palmitic acid molecule in a slightly expanded film so that the point of attachment appears to be only one. The following position of the molecule of the dye-stuff on the water surface is quite likely.

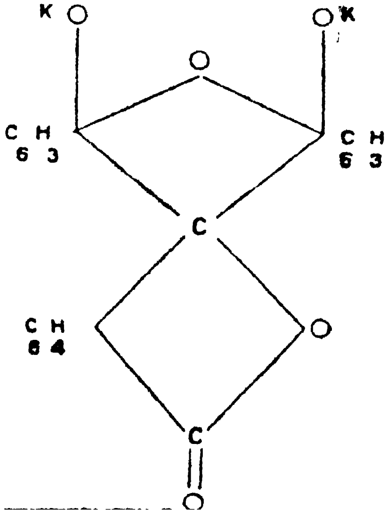

FIG. 2.

Similarly a standard solution of methyl violet was also prepared. The area per molecule in the film that spread on water was found to be 180×10^{-16} sq. cm., somewhat larger than in the case of the very complicated penterythritoltetrapalmitate molecule[17] which has several points of attachment (or polar heads) to the water surface. The film obtained was a liquid film which was swept out by a trace of oil and sent into the water. The following figure shows a probable arrangement with four points of attachment to the water surface.

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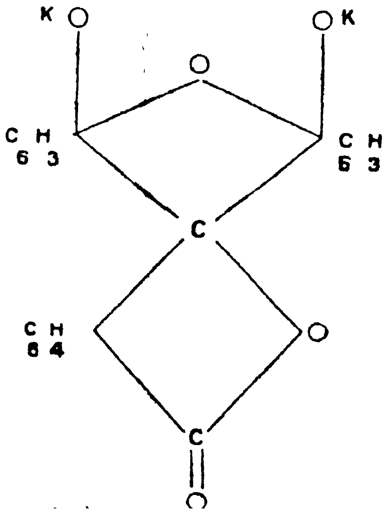

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The carbon atom at the top is linked to the three benzene rings each with the substituted $N(CH_3)_2$ group in contact

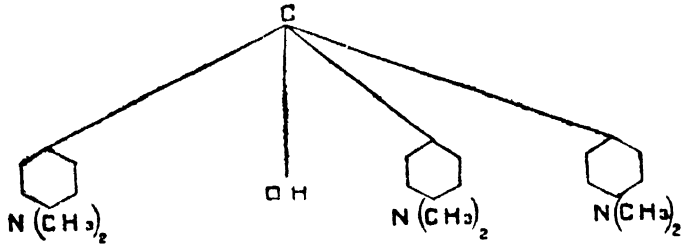

FIG. 3.

with the water. The thickness of the film comes out as nearly 3×10^{-8} cm. and has the same order of magnitude as the diameter of the benzene ring.

As a result of the observations with various substances in contact with the surface of water, it was found that almost in every case the solution of the substance in the water below took place more efficiently at the surface by the process of *surface solution* and subsequent *internal solution* of the spread material. When the substance was kept under the surface, even after a long time, it was found that most of the substance had been clinging to the platinum loop. When the loop was again brought in contact with the surface, the substance spread quickly and then disappeared into the water below.

(*d*) *Measurement of the velocity of spreading.*—

The velocity of spreading for various substances was measured by the following method. (Fig. 4)

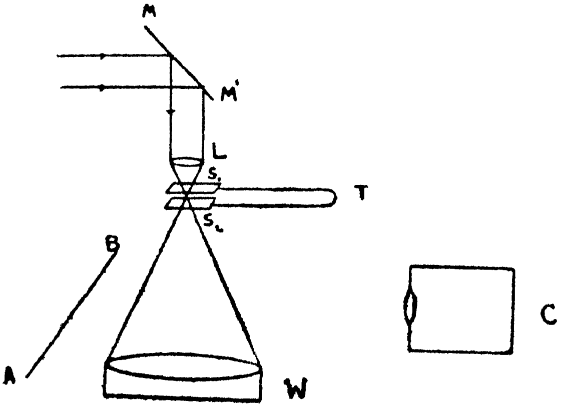

FIG. 4.

M M^1 is a small mirror reflecting down vertically a beam of sun-light which is focussed on the plane of contact of two Gillette razor blades S_1 S_2. These blades are attached to the prongs of the electrically maintained tuning fork T. The blades cover each other when the fork is at rest and periodically open out allowing the focussed beam to pass through and illuminate the surface of the water in the vessel W. The lens L has to be very good as otherwise uniform illumination cannot be obtained. The Zeiss cinematograph lens was used for this purpose. The films allowed to spread on the surface of water in W push out small semi-circular strips of white paper allowed to float on the surface near the point of application of the film in the loop. The paper strips were free from any trace of oil and, being periodically illuminated, show up as isolated images in their actual paths. The water surface is provided with a dark background by placing a sheet of black paper under the vessel W and is reflected by means of the mirror AB into the camera. From the negatives taken, the distance between the successive images of the paper strip can be easily measured, and knowing the actual diameter of the strips, the magnification and the frequency of the fork ($n=24$), the velocity of the spreading film at different intervals can be calculated. These records have been taken for a large number of substances and the results tabulated in Tables I and II. The velocity is initially high for all substances, but rapidly diminishes in proportion to the solubility and volatility of the substance used. If the substance is insoluble and non-volatile the velocity is constant over several centimetres.

TABLE I.

Substance.	Formula.	Remarks.	Distance traversed in ½ second in cms.	Initial Velocity in cms. sec.
Methyl alcohol ...	CH_3OH	The area of spreading is small for Methyl and goes on increasing rapidly while going up the series.	1·82	10·0
Ethyl alcohol ...	C_2H_5OH		1·77	8·7
Propyl alcohol ...	C_3H_7OH		4·3	18·7
Butyl alcohol ...	C_4H_9OH		4·3	21·8
i-Butyl alcohol ...	C_4H_9OH		2·5	8·8
Allyl alcohol ...	C_3H_5OH		2·4	10·0
Amyl alcohol ...	$C_5H_{11}OH$		3·2	12·5
Octyl alcohol ...	$C_8H_{17}OH$		3·4	11·4
Formic acid ...	HCOOH		1·7	8·7
Acetic acid ...	CH_3COOH		2·9	15·4
Propionic acid ...	C_2H_5COOH		3·95	17·5
Butyric acid ...	C_3H_7COOH		4·14	15·6
Pentane ...	C_5H_{12}	Very small spreading.	...	...
Allyl chloride ...	C_3H_5Cl	The bromide spreads very much less than the chloride.	...	...
Allyl bromide ...	C_3H_5Br		...	...
Benzene ...	C_6H_6	Spreads very little (say 1 mm.).	...	...
Benzyl chloride ...	C_6H_5—CH_2Cl	A drop spreads and rapidly sends out droplets which spread as thin films.	...	...
Chloro-benzene ...	C_6H_5—Cl	Spreads rapidly behaving like amyl alcohol (amoeboidal).	...	...
Bromo-benzene ...	C_6H_5Br	Very small spreading—very slightly amoeboidal.	...	...
Nitro-benzene ...	$C_6H_5(NO_2)$	Spreads very rapidly into thick film from the edges of which mono-molecular spreading occurs rapidly.	...	...
Toluene ...	$C_6H_5CH_3$	Spreads more than benzene.	...	...
Carbon-bisulphide ...	CS_2	No spreading observed	...	...
Cyclohexane ...	$C_6H_6\ H_6$	No spreading	...	...
Carbon-tetrachloride ...	$C\ Cl_4$	No spreading	...	...

TABLE II.

Substance.	Formula.	Remarks.	Distance traversed in ¼ second in cms.	Initial velocity in cms. sec.
Antipyrin ...	$C_{11}H_{12}ON_2$	Violent movements, soluble	2·3	12·5
αNaphthol ...	$C_{10}H_8O$	Moderate movements, soluble.	...	...
Salol ...	...	Disintegration into fine crystals, not soluble.	...	...
Resorcin ...	$C_6H_6O_2$	Violent movements, soluble	2·1	10·6
Acetanilid ...	C_8H_9ON	Violent movements	...	...
Succinic acid ..	$C_4H_6O_4$	Moderate movements		...
Acetoxime ...	C_3H_7ON	Brisk movements, soluble	...	...
Ethyl Carbaminate ...	$C_2H_5N{\equiv}C$	Violent movements, soluble	3·1	12·0
Camphor ...	$C_{10}H_{16}O$	Brisk movements, soluble	1·3	5·0
Propylamin Hydrochlorate.	...	Violent movements, soluble	2·2	9·0
		Dye stuffs.—		
Methyl violet ...	$C(OH)[C_6H_4N(CH_3)_2]_3$	Violent movements, remarkable spiral movements—movements persist long as the spread film is a liquid film.	...	...
Tetriod fluorescein ...	...	Movements last for the short time taken to form the solid film and are not very striking.	1·9	8·8
Fluorescein ...	...	T	...	...
Eosin ...	...	T	...	...
Turquoise Blue ...	...	M	...	...
Brilliant Green ...	...	M	...	...
Alizarin Cyanin ...	...	T	...	...

M—behaves like methyl violet.

T—behaves like tetriod fluorescein.

TABLE II—(*Continued*).

Substance.	Formula.	Remarks.	Distance traversed in ¼ second in cms.	Initial velocity in cms./sec.
Gentianaviolet ...	...	M	...	...
Methyl Green ...	...	M	...	...
Carmin ...	...	T	...	...
Anilin—red ...	...	T	...	...
Anilin—blue ...	...	T	...	...
Dahlia ...	...	M	...	...
Erythrosin ...	...	T	...	...
Haematoxiline ...	...	Not very active ...	...	...
Bismark—brown ...	...	Slightly active ...	...	...

M—behaves like methyl violet.
T—behaves like tetriod fluorescein.

6. *Surface Tension of Spreading Films.*

To understand the influence of these spreading films on the mass of the material either in the form of a liquid lens or a solid particle the following experiment was performed.

A brass trough (of dimensions 18″ by 4″ by 3″) (see Fig. 5) whose edges at the top were nicely planed was completely filled with water and two glass blocks slightly longer than the width of the vessel and initially in contact with each other, were drawn apart so as to scrape the water quite clean at the centre. The pointer P of the balance consisted of a thin long blade of pine wood with its plane parallel to the width of the vessel. A mica sheet with its lower edge half a centimetre above the surface of water was attached to the lower end of the pointer P. The float was a rectangular piece of pine-wood with its flat bottom resting on the surface and its upper surface sloping down from the thick end A towards the thin edge B. The float was held loosely against the mica sheet by a couple of pins on either side mounted so that there was no thrust exerted by them and the float against the pointer. If the balance was then set free, the pointer began to oscillate along with the float to and fro without much damping. The balance, by the suitable adjustment of weights on the beam above the knife-edge at the centre and on the scale-pans, was rendered sensitive enough to indicate a difference in weights on the pans as small as 5 mg. To indicate the deviation of the float from its position of rest, a pin was fixed to the edge of the trough so that its point nearly touched the near end of the mica sheet. The water was scraped a number of times and the float wetted with water and fed with a few drops of amyl alcohol so that the edge was uniformly fed with the liquid flowing down to B. As soon as the edge B began to receive alcohol, the latter began to spread vigorously towards D and the float along with the pointer was deflected through a definite angle

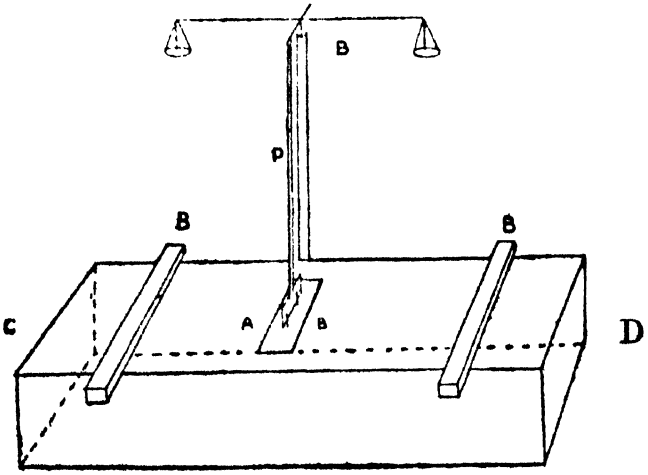

FIG. 5.

towards C. This is evidently due to the steady difference between the surface tension of the clean water surface on the side C and that of the spreading film on water on the side D. The weight added to the left-hand scale-pan to bring back the mica sheet to the position of rest was carefully adjusted and noted. If l be the length of the arm of the balance and L the length of the pointer up to the water surface, then $\frac{l}{L} \times wg.$ gives the force in dynes acting at right angles to the edge A in the direction D C horizontally. This force per centimetre length of the float indicates the actual steady force acting per centimetre of the edge when spreading occurs from only one side. If the spreading was made to take place from both the edges A, B by using a float sloping towards both A and B from the thicker centre, no movement of the float took place. On the other hand, if the edge A was V-shaped (with the angle inwards), the pointer was moved towards D indicating that the surface tension of the film in front of A was lower. As the angle of the V was diminished slowly, the difference in tension goes on increasing until the angle is about 45°. Further diminution had no perceptible influence.

With solid substances there is some difficulty in doing the experiment, except in the case of camphor. Large blocks of camphor are easily available. These blocks were dipped in molten paraffin. After the paraffin had solidified, first one edge was scraped free from paraffin to allow spreading from that edge. The camphor block was then substituted for the float and, when the water was scraped clean, a deflection was observed away from the direction of spreading. The weight necessary to counterbalance was noted and then both the opposite edges were freed from paraffin. Then spreading took place from both the edges and no deflection was noticed. One side was then cut into a V-shape, when the pointer was deflected away from the V side. The deflections were also observed for many other liquids. The important point to note is the influence of the shape of the boundary on the nature of the spreading film and the surface tension forces acting on the float. One finds that the floating body is not in equilibrium unless its shape is symmetrical and the distribution of the stream lines is therefore symmetrical. The results for camphor and amyl alcohol are given below :—

Substance.	Shape of boundary from which spreading takes place.	Force acting on float per cm.
Camphor	Square piece spreading from one side only.	6·2 dynes.
	Spreading from both sides, one side being V-shaped.	1·4 ,,
Amyl alcohol ...	Spreading from one side only ...	30·0 ,,
	Spreading from both sides one side being V-shaped.	6 ,,

7. *Theory of the Movements.*

We are now in a position to attempt an explanation of the movements. It is evident that the only causes which can give rise to the movements are :—

1. A mechanical recoil and
2. Differences in the surface tension forces acting at the boundary of the floating material due to the non-uniform distribution of the stream lines.

We have already established that this depends on the shape of the line of contact of the substance with the water surface.

Let us consider the ideal case in which spreading from the parent substance takes place only as a monomolecular film and the substance receives no additional deformation. We have already remarked that in such cases the velocity and mass of the spreading film are too small to account for the observed movements. Even if this were not the case we can dismiss the effect of recoil by the following considerations.

Let us assume that the mass of the material removed is proportional to the length of the boundary (line of contact with the water surface) and that the spreading from any element of the edge is normal to the edge. If an element of length δl is considered, the amount of material removed by spreading is proportional to $\delta l \times v$, where v is the velocity of the spreading film. In our experiments with the velocity of the spreading films the velocity was found to be fairly uniform in all directions. The recoil momentum of the particle itself in the opposite direction so far as this element is concerned is $\delta l \times v \cos \theta$ where θ is the angle between the normal to the edge and the actual direction of movement of the parent substance. If one divides the whole body into two parts by a line at right angles to the direction of movements and balance the resultant momenta of the two parts, one would find that they exactly balance. This may be easily seen in the case of a semi-circular body. Here the movement is away from the straight edge. The momentum against the straight edge is proportional to $2r \times v$ where r is the radius. For the semi-circumference the momentum is

$$2rv \int_0^{\frac{\pi}{2}} \cos \theta d\theta = 2rv.$$

We thus see that recoil cannot account for the movements of substances in which the spreading on water is in monomolecular films. This condition holds for all the transparent crystalline organic compounds like camphor, antipyrin, etc., and the fatty acids.

On the other hand the density of the spreading film or the packing of the stream-lines or lines of flow of the molecules would depend largely on the shape of the boundary. In front of concavities the film would travel much further out as the stream-lines are focussed, as it were, and the surface tension would receive a steady lowering over a large distance whereas in front of projections the stream-lines rapidly diverge out and get further apart very soon. At such places the lowering of the surface tension would necessarily be less and so the substance, unable to remain in equilibrium, moves away from the concave side. In fact, we have already measured such steady differences in the surface tension forces acting at the edges of camphor pieces of various shapes. Such differences of the surface tension would produce the accelerated motion of the substance when left free to move. This has been actually verified in the case of a rectangular strip of paper coated at one edge with a trace of oleic acid and left to move on a very clean surface of water. The velocity of the paper strip was measured by the method described in an earlier section. The velocity was an accelerated one, the acceleration being 26 centimetres per second corresponding to a difference in surface tension of ·917 dyne per centimetre, the mass of the paper strip being ·035 gr.

Amyl Alcohol.

Let us apply these ideas to the case of amyl alcohol lenses on water. It is a fact of observation that the deformation of the lens is due to some sudden and spontaneous force acting at a selected spot very near the lens. If we first consider a single lens floating on water, the spreading film surrounding the lens occupies the rest of the surface whereas actually we have a large number of lenses each surrounded by spreading films of much smaller area. The spreading films still leave the lenses with practically the same speed but, unable to spread further owing to the presence of other lenses, they go with a large velocity into the water at the edge of the circle of spreading in the form of streaks. These streaks of dissolved alcohol are visible to the naked eye against a white back-ground. They are lighter than water and tend to curl up and approach the surface again. The subsequent movement of a lens depends mostly on the disposition and number of these solution streaks just below the surface as they produce a non-uniform distribution of the concentration of the alcohol in water. This non-uniformity facilitates more rapid solution of the spread film at some places than at others, which, in turn, produces increased spreading from the lens in the direction of more rapid solution. This uni-directional spreading produces a recoil at the edge and deforms it slightly in the oppsite direction producing a concavity. This initial deformation is just what is necessary to produce increased spreading from that place and produce, in addition to the continuously accelerated recoil of the edge, lowering of the surface tension just in front of it. The lens experiences, therefore, a quick translational movement as a whole away from the deformed side. The rapid uni-directional spreading from the deformed edge may be observed by the rapid going down of solution streaks in the neighbourhood. This going down can always be observed and takes place whenever the lens is deformed and always very near to the deformed edge (as the films do not spread out very far when there are a large number of lenses on the surface).

Once the effect of solution stops the movements depend only upon evaporation. The activity depending on this is very much less and may be similarly explained.

The Dye-stuffs.

In the case of the dye-stuffs, as we have described before, the spreading from the solid crystal takes place not as a uniform mono-molecular film, but as the shooting out of innumerable small microscopic crystals at a rapid rate, these crystals later dissolving at a distance from the crystal. This streaming out of the crystals does not take place with the same strength from different parts of the edges. This gives a resultant recoil momentum to the big crystal which contributes to a large extent to movement in the backward direction.

The surface-tension differences which may be produced as a result of the non-uniform streaming would also contribute to movement in the same direction as the recoil; but experiments with methyl violet and other similar dye-stuffs convince one that in these cases the recoil effects are mostly responsible for the movements. The clear areas surrounding the crystals are quite transparent when seen in the ordinary way showing that no appreciable solution is taking place in that region to reduce the surface tension. The crystal streams are reponsible for keeping the dissolved film outside at a distance and keeping the surrounding space clear, thereby preventing the film outside from acting on the crystal. This state of affairs is, however, just the *reverse* of what takes place in the case of mono-molecular spreading from lenses of oleic acid, amyl alcohol, camphor, etc., where the films are densely packed near the source but get more and more *expanded* at a distance from the liquid lenses or the crystals as the case may be.

The movements shown by substances like tetriod-fluorescein which spread as solid films on water last only until the film has had time to spread and adjust itself into a solid film. They are produced just in the same way as in the case of methyl violet, but, due to the much larger resistance offered to the movements by the solid film, are soon stopped.

8. *Optical Study of Monomolecular Films.*

In a recent paper[18] the increase in the scattering of light by the surface, when a clear surface of water is covered with a mono-molecular film of oleic acid, has been described and photographs illustrating the effect reproduced. Similar brightening up of the opalescent spot occurs when transient or permanent films of the various substances are formed on the surface of clear water.

To observe the scattering a tall beaker blackened completely outside is filled to the brim with distilled water comparatively free from motes. After allowing all traces of oily matter to rise to the surface, the top layer is blown off suddenly and the clear surface thus obtained placed at the focus of a beam of sun-light incident at 45° and passing through a lens. The eye is protected from the light reflected by the water surface by a suitably placed black screen provided with a small hole. The scattered light adjacent to the reflected beam is observed through the aperture. The surface opalescence then appears like a greyish-white cap terminating the bluish-white internal track. When the eye is held in a fixed direction by observing through two small apertures, changes in the intensity depending upon the angle of observation may be completely eliminated. While the eye is steadily viewing the opalescent spot, if the surface is touched with a platinum loop containing a film of any one of the organic compounds mentioned in Table I, an increase in the scattering may be readily perceived. This lasts only as long as the spreading takes place as the films later dissolve or evaporate away. The higher alcohols and those liquids in general having a high refractive index produce a large increase in the scattering. Camphor and some of the other solids like antipyrin show similar increase of scattering when their monomolecular films are spreading. Sometimes, however, if the crystals had not been prepared carefully dust particles entrapped in the solid occasionally leave the crystal and cross the spot. Owing to the experimental difficulties, the actual measurement of these intensities has not been attempted.

In the case of the dye-stuffs, however, the corresponding phenomena are of very great interest. Here the films are more permanent and may be studied more leisurely. It may be noted, however, that when we deal with these films, as there is no regular streaming or renewal of the film, focussing a strong beam of sun-light melts away the film so that one can expose the surface to the light only for a few seconds at a time. In case the film is melted, the vessel may be moved slowly to bring a fresh part of the film into view.

When a mono-molecular film of methyl violet is produced on a fresh surface of water by allowing a small quantity of its aqueous solution to spread on the water, the scattering of light by the film is no longer greyish-white, but a faint *yellowish-orange* (of the same tint as the light reflected by the surface of the dry crystal surface). The intensity of this spot is roughly twice or thrice that of the pure water surface. If more of the solution is placed on the surface, it quickly goes into the water below and then the internal track appears pink, while the surface continues to have the feeble orange-yellow scattering.

In the case of the Fluorescein group of dye-stuffs, *viz.*, *tetriod* fluorescein, Eosin, Erythrosin, etc., the mono-molecular films obtained by the spreading of small quantities of the respective solutions, give very intensely green (the intensity is several hundred times that of the pure water surface) fluorescent spots. The transmitted beam is visibly coloured owing to the absorption by the *mono-molecular* film. It is, indeed, very interesting that one can observe directly the absorption by such thin films.

9. *Summary and Conclusion.*

The movements of small particles of camphor, antipyrin and a large number of soluble organic compounds on water are commonly explained as recoil effects or as due to differences in the rate of solution of the substance at various points over the boundary. In this paper a different theory in which the movements are related to the form of the stream-lines of flow of the material along the surface is put forward.

Most organic compounds, whether *solid* or *liquid*, when brought in contact with a clean surface of water, spread as mono-molecular films. These films quickly disappear by solution or evaporation. When a large quantity of the substance (as a lump or lens as the case may be) is present, the spreading is continuously maintained. Streams of the material leave the edges and the stream-lines are found to be convergent when the boundary is concave and divergent when it is convex. In the former case the surface-films are denser and their tension smaller than in the latter case, as shown by actual measurement. As a consequence, forces are set up which cause the dissolving particle or droplet to move away from the concave boundary.

For example, when lenses of amyl alcohol float on water, they are found to distort in shape and to move away from the concave side, the movements, however, stopping when the water below gets saturated and evaporation is prevented. Similar effects are observed with camphor blocks having concave edges on one side and with paper strips of similar shape moistened with amyl alcohol or even oleic acid.

In the case of particles of dye-stuffs thrown on clean water, it is found by microscopic observation that *micro-crystals* of appreciable size are rapidly shot off from particular points on the boundary. In this case the movements of the parent crystals are due to recoil and often exhibit beautiful spiral forms. Some dye-stuffs such as methyl violet produce liquid films and exhibit rapid movement while others, such as tetriod fluorescein give solid films which do not permit such rapid movements of the crystal. When touched by an oiled wire, a liquid film of dye-stuff is swept off but a solid film exhibits radiating cracks. A particle of dye-stuff, when thrown on a surface of water contaminated by oil, refuses to spread and immediately sinks leaving behind a beautiful trail.

Mono-molecular films on water are made visible directly by the increased light-scattering power of the surface and in some cases as for instance, tetriod fluorescein, by the intense fluorescence under strong illumination. The transmitted beam is visibly coloured owing to absorption.

The present investigation was carried out at the Indian Association for the Cultivation of Science. The author's best thanks are due to Prof. C. V. Raman, F.R.S., who suggested the work and took much interest in its progress.

Description of Plates :—

Plate I, *A*, *B*, *C* and *D* show the successive movements of amyl alcohol drops on water. The series of pictures run from right to left continuously from *A* to *D*.

Plate II, Figs. 1, 2, 3 and 4 illustrate the spiral movements of methyl violet crystals on a water surface.

Plate III, Fig. 1 shows the trails of methyl violet crystals sinking down when the water surface is oily.

Fig. 2 shows the trails of tetriod fluorescein particles sinking down when the water surface is oily.

Fig. 3 shows the trails in (1) when they begin to diffuse slowly sideways.

Fig. 4. A cracked solid film of tetriod fluorescein when touched by an oiled wire.

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2

Are Gaseous Molecules Orientated in a Magnetic Field?

BY

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Introduction.

Glaser,[1] working on the diamagnetic susceptibilities of hydrogen, nitrogen and carbon dioxide at low pressures, has obtained some very interesting results. As the pressure is gradually lowered, the susceptibilities decrease proportionately only up to a certain pressure which depends on the nature of the gas and, to some extent, on the value of the magnetic field. Below this point the susceptibilities are greater than, and approach at low pressure three times, the value one would expect if the original rate of decrease with pressure had been maintained throughout. With slightly improved apparatus he has later[2] extended these observations to the case of carbon monoxide, which is also diamagnetic.

Glaser explains these "anomalies" by assuming that there is a tendency for the molecules to set themselves in a definite direction under a magnetic field and that this setting would require some time owing to the moment of inertia of the molecules. The effect of collisions would be to hamper this setting up. Hence so long as the time between two collisions is small in comparison with the time required for the molecules to set themselves, there will be no orientation of the molecules; and this will be the case at the higher pressures. But when the pressure is lowered, the time between two collisions begins to be comparable with the time of setting of the molecules and orientation will appear and consequently an increase in susceptibility. The orientation will, however, be complete only when the time between two collisions becomes large; this will correspond to the low pressures where the susceptibilities are again proportional to the pressure.

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[1] Ann. der Physik, 75, 459, 1924. See also Physik. Zeits., 26, 212, 1925,

[2] Ann. der Physik, 78, 641, 1926.

Thus the orientation theory explains in a simple way the observed facts. But probably the strongest argument in its favour is the natural explanation it offers for the three-fold values of the apparent molecular susceptibilities at low pressures; this is actually the ratio of the value of the susceptibility when the molecules have all set themselves in any particular direction, to the value when they are orientated at random.[3]

Also Glaser finds that the actual pressures at which the anomalous values begin to appear for the different diamagnetic gases investigated, can be expressed as an empirical function of the moment of inertia of the respective molecules; which seems further to support the orientation theory.

However, there are some real difficulties in accepting the theory. For instance, it is reasonable to suppose that all the molecules above—H_2, N_2, CO and CO_2—possess an axis of symmetry, *viz.*, the line joining the atomic nuclei. "Owing to the relatively large mass of the nuclei, it is only about the line joining them that the molecule will acquire an appreciable magnetic moment under the influence of the field."[4]

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[3] Stoner, *Nature*, 115, 302, 1925.

[4] Stoner, *loc. cit.*

If Glaser's factor 3 is to be explained, these nuclear axes, which previously were orientated at random, should all point in the same direction on the introduction of the magnetic field. This cannot be reconciled with the existence of rotation of the molecules about axes perpendicular to their axes of symmetry, required by the theory of specific heats, etc.

Hence it would be extremely instructive to verify by independent methods whether there is real orientation of the molecules under the conditions of Glaser's experiments. Such methods are not difficult to devise.

Double refraction.

For instance, if there is actual orientation of the molecules in a magnetic field, then owing to their optical anisotropy, the medium will become doubly refracting. We can calculate the magnitude of this effect.

Let us take for example the case of carbon dioxide at 50 mm. pressure; at this pressure it is evident from Glaser's curves that the orientation, if any, of the molecules should be complete. When there is orientation, the line joining the C- and the two O-nuclei, which we might call the axis of the molecule, will set itself parallel to the field.

Now let μ be the normal refractive index of carbon dioxide, *i.e.*, the refractive index when the molecules are orientated at random; and let $\mu\|$ and $\mu\perp$ be the refractive indices, when the CO_2-molecules are all orientated with their axes along the magnetic field, for vibrations parallel and perpendicular respectively to the magnetic field.

Also let A, B be the optical moments induced in a molecule of CO_2 per unit light vector incident along and perpendicular to its axis respectively.

Then according to its usual theory of dielectric polarisation, remembering that, for the small pressures we are considering, the μ's are very nearly equal to unity, we have

$$\begin{aligned} \mu_{\|}-1 &= 2\pi\nu.\mathrm{A} \\ \mu_{\perp}-1 &= 2\pi\nu.\mathrm{B} \\ \text{and} \qquad \mu-1 &= 2\pi\nu.\frac{\mathrm{A}+2\mathrm{B}}{3} \end{aligned} \qquad (1)$$

where ν is the number of molecules per unit volume.

Now $\frac{\mathrm{A}}{\mathrm{B}}$ can be calculated from measurements on light-scattering. According to Rayleigh's theory[5] of scattering by anisotropic molecules, the ratio of the components of the transversely scattered light is given by

$$r=\frac{2(\mathrm{A}^2+\mathrm{B}^2-2\mathrm{AB})}{4\mathrm{A}^2+9\mathrm{B}^2+2\mathrm{AB}} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

For carbon dioxide, taking $r=\cdot107$ (mean of the values ·117 of Rayleigh,[6] ·106 of Raman and Rao[7] and ·098 of Cabannes and Granier[8]) we get from (2)

$$\frac{\mathrm{A}}{\mathrm{B}}=2{\cdot}41.$$

This agrees well with the value 2·42 calculated by Ramanathan[9] from the structure of the CO_2-molecule and does not differ much from the value 2·15 calculated from the Kerr constant measurements of Hansen[10] and Szivessy.[11]

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[5] Phil. Mag., 35. 373, 1918. Collected papers, Vol. VI, p. 540.

[6] Proc. Roy. Soc., A, 97, 435, 1920.

[7] Phil. Mag., 46, 426, 1923.

[8] Journ. de Physique, VI, Series, Tome IV, p. 429, 1923.

[9] Proc. Roy. Soc. A, 107, 684, 1925.

[10] Quoted by Szivessy, Jahrbuch der Radioaktivität, 1920.

[11] Zeits. f. Phys., 26, 342, 1924.

For the room temperature, *viz.*, 225°C, and 50mm. pressure, we have from the tables, for the sodium light,

$$\mu-1=2{\cdot}71\times10^{-5}:$$

so that, using (1) and (2) we get

$$\mu\|-1=4{\cdot}44\times10^{-5}$$

$$\mu\perp-1=1{\cdot}84\times10^{-5}$$ [12]

Thus supposing a beam of plane polarised light traverses carbon dioxide perpendicular to the magnetic field, if the vibrations are parallel to the field, there will be a path retardation of $1{\cdot}73\times10^{-5}$ cms., *i.e.*, about 0·3 of a wavelength of sodium light for each centimetre length of path across the magnetic field; while vibrations perpendicular to the magnetic field will be accelerated by about 0·15 of a wavelength per centimetre of path.

The author used an interference arrangement in which one of the interfering beams traversed a tube of carbon dioxide lying between the flat pole-pieces of an electromagnet, perpendicular to the magnetic field, while the other traversed a similar tube of carbon dioxide, in communication with the first, placed outside the field. The second tube served merely as a compensator. White light was incident and the

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[12] Similar calculation gives the following values for the other gases (at 25°C and 50 mm. pressure) :—

	$\mu-1$	$\mu\|-1$	$\mu\perp-1$
Hydrogen	$0{\cdot}838\times10^{-5}$	$1{\cdot}14\times10^{-5}$	$0{\cdot}687\times10^{-5}$
Nitrogen	$1{\cdot}80\times10^{-5}$	$2{\cdot}48\times10^{-5}$	$1{\cdot}46\times10^{-5}$
Carbon monoxide	$2{\cdot}02\times10^{-5}$	$2{\cdot}71\times10^{-5}$	$1{\cdot}67\times10^{-5}$

The values refer to the sodium line.

interference fringes were observed through a micrometer eye-piece and a nicol.

The field between the pole pieces was estimated at about 10,000 gausses, and it was fairly uniform over a diameter of about 8 cms.

With this arrangement and with the nicol rotated for transmitting vibrations parallel to the magnetic field, if there is complete orientation of the molecules on putting on the field there should be a shift, at 50mm. pressure, of the interference system, by more than two fringe-widths. For perpendicular vibrations, the shift should be in the opposite direction by more than one fringe-width.

However in the actual experiment there was no shift for either of the components, even though a shift of a tenth of a fringe-width could easily have been detected. A preliminary experiment was performed with carbon dioxide from a commercial cylinder at various pressures from 1 atmosphere down to about 10 mm. of mercury and the experiment was repeated afterwards with pure dry carbon dioxide with entirely negative results in both cases.

There is another familiar form in which the double refraction, if any, could be detected, *viz.*, to allow light polarised at an angle of 45° to the magnetic field to traverse the tube of carbon dioxide lying between the pole-pieces of the magnet and to extinguish the transmitted light with a crossed nicol. For unit length of track across the field, in carbon dioxide at 25°C and 50 mm. pressure, the vibrations perpendicular to the magnetic field will gain in phase about $0{\cdot}9\pi$, over the vibrations parallel to it, so that when the field is put on, there should be a restoration of light, the actual illumination of the field of view varying as the pressure is gradually altered.

The experiment was tried with carbon dioxide at different pressures down to about 10 mm. of mercury, with a tri-field

Lippich polariser and a nicol; and there was no restoration of light when the magnetic field was put on.

It need hardly be pointed out that the partial orientation of the molecules in the field, due to the differences in their magnetisability along and perpendicular to their axes, which will be determined by Boltzmann's theorem, will be very small; and the double refraction arising therefrom (the Cotton-Mouton effect) will be entirely negligible.

Light-scattering.

We have another very interesting method of studying the orientation of molecules, which, however, is not so delicate as the above methods. Suppose a beam of light is traversing any medium perpendicular to a magnetic field, and the light scattered perpendicular both to the track and to the magnetic field is examined.

Taking carbon dioxide again, in the absence of the magnetic field, when the molecules are orientated at random, owing to the optical anisotropy of the CO_2-molecules, the scattered light is imperfectly polarised, the ratio of the components being, as already mentioned, equal to ·107. But suppose the magnetic field is put on and all the CO_2-molecules set themselves with their axes along the field. Then from the theory of scattering by anisotropic molecules it is obvious that none of the molecules in the field can give rise to vibrations along the incident light. Also the vibration in the scattered light, parallel to the magnetic field, will be entirely due to that component of the incident unpolarised light which is vibrating in the same direction, *i.e.*, vibrating along the axes of the CO_2-molecules. Thus, when the field is put on, the transversely scattered light will become *perfectly polarised* with its vibrations parallel to the field. But the total intensity will not be appreciably altered because according to the Einstein-Smoluchowski expression the ratio of the intensities before and after the introduction of the field will be equal to

$$\frac{(\mu-1)^2 \cdot \frac{6\,(1+r)}{6-7r}}{\frac{1}{3}\,(\mu_{\parallel}-1)^2}$$

which, on evaluation is found to be very nearly equal to 1[13].

The scattering by carbon dioxide was studied in the usual way ; the gas was contained in a glass cross of about 1·8 cms. diameter, and the transversely scattered light was examined through a double-image prism adjusted to transmit vibrations parallel and perpendicular to the incident track. At a fourth of an atmosphere there was no change in the depolarisation in a field of about 4,000 gausses. When however the pressure was further reduced, though the stronger component was distinctly visibie even at a tenth of an atmosphere, the weaker component could not be recognised clearly, as the imperfections in the background, particularly the light diffused from the edges of the apertures used inside the cross, became conspicuous. Hence it was not possible to test whether the weaker image disappears at still lower pressures, when the field is put on. The author hopes to repeat the experiment with a bigger glass cross and under better conditions.

Paramagnetic Gas.

In the later work mentioned, Glaser has also investigated the paramagnetic gas oxygen and he finds that over the whole range investigated, *viz.*, from 16 atmospheres down to about 20 mm. the susceptibility is always proportional to the pressure. He explains the absence of anomalies similar to those observed for diamagnetic gases by remarking that, with the magnitude of the paramagnetic moment one should expect the anomalous region only at very high pressures; which means that a paramagnetic gas at ordinary pressures corresponds to the last stage in a diamagnetic gas where the molecules are completely orientated along a particular direction.

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[13] In the cases of hydrogen, nitrogen and carbon monoxide the total intensity is slightly diminished (is about 0·8 to 0·9 times).

But actual experiments with oxygen at different pressures down to less than 10 mm. of mercury, by the interference method, failed to detect any double refraction in a field of about 10,000 gausses.[14] Again light transversely scattered by the gas at atmospheric pressure failed to show any change in its depolarisation in a field of about 4,000 gausses.

On the other hand, some recent experiments by Debye and Huber [15] on nitric oxide and other substances seem to throw doubt even on the existence of the partial orientation of paramagnetic molecules in a magnetic field required by Langevin's classical theory, not to talk of any complete orientation.

Summary and Conclusion.

Glaser has observed some "anomalies" in the diamagnetic susceptibilities of gases at low pressuses; which he explains by assuming that the molecules, under these conditions set themselves in a particular direction in a magnetic

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[14] For oxygen at atmospheric pressure and 25°C.

$$\mu-1=2{\cdot}48\times10^{-4}$$

$$\mu_{\parallel}-1=3{\cdot}91\times10^{-4}$$

and $$\mu_{\perp}-1=1{\cdot}77\times10^{-4}$$

for sodium light. For 8 cms. of path across the field, as was the case in the actual experiment, if there had been complete orientation, there should have occurred a shift of the interference system by

$$\frac{8{\cdot}(3{\cdot}91-2{\cdot}48){\cdot}10^{-4}}{5{\cdot}89\times10^{-5}}$$

or 20 fringe-widths for vibrations parallel to the magnetic field and by 10 fringe-widths, in the opposite direction, for vibrations perpendicular to the magnetic field.

[15] See Debye, Zeits,, f. Phys. 36, 300, 1926.

field. The present paper describes some experiments which failed to show any such setting up of the molecules. Thus an interference method failed to detect any change in refractive index when a magnetic field was put on; with the gas between two crossed nicols there was no restoration of light in the field; and the depolarisation of the transversely scattered light did not show any change in the field.

The actual magnitudes of the effects to be expected, according to the orientation theory, in the above experiments, are calculated and are found to be far too large to escape detection in case they existed.

Our uniformly null experiments lead therefore to the conclusion that the molecules are not orientated in a magnetic field under the conditions of Glaser's experiments and that we have to look for an explanation of the " anomalies " observed in the diamagnetic susceptibilies of gases at low pressures elsewhere.

The author wishes to thank Professor C. V. Raman who suggested the work and took great interest in its progress.

3

" Clement and Desorme's Experiment "—A problem on efflux of gases.

By

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Abstract.

In a form of apparatus for the determination of the ratio of specific heats of air, from measurement of pressures it is generally assumed that equalisation of pressure takes place instantaneously. The time necessary for such an equalisation is calculated by simple mathematical means, in terms of known data. The results so calculated are found to agree closely with experimental values. The effect of either over or undershooting this interval is studied at some length and practical suggestions made.

Introduction.

In a common form of apparatus for the determination of ratio of specific heats, air is initially compressed into a pretty large carboy provided either with a stop-cock or a stoppered mouth piece. As is well known, if P_0 is the pressure initially within the carboy, P that of the surrounding atmosphere with which the carboy is "momentarily" kept in communication and P_1 the final pressure, it is shown that:

$$\gamma=\frac{\text{Log } P_0-\text{Log } P}{\text{Log } P_0-\text{Log } P_1} \qquad \ldots \quad (1)$$

This result assumes that at the instant when the stop-cock is closed there is exact equalisation of pressure—an assumption not easily to be fulfilled in actual practice.[1]

When a compressible fluid is allowed to flow into an unlimited space at a lower pressure, *finite* interval elapses before exact equalisation of pressure is attained, depending on the size and shape of the orifice, the volume of the chamber and the pressure difference. The accuracy of the result depends exclusively on the fulfilment of this condition and is much vitiated if the communication is cut off either a little too soon or too late. It is evident from the above equation that if the stop-cock be closed too soon, that is, before the pressures are equalised the final pressure P_1 is greater owing partly to unescaped air and the value for γ is certainly higher than otherwise; for, let the stop-cock be closed when the pressure is P' ($>P$), that is, before P is reached.

Let T_0 be the initial temperature and T the instantaneous temperature on adiabatic expansion if the pressure falls to that of the surrounding atmosphere; we have

$$T=T_0\left(\frac{P}{P_0}\right)^{\frac{\gamma-1}{\gamma}} \text{ and in addition } P_1=P\left(\frac{T_0}{T}\right)$$

$$\therefore \quad \frac{T}{T_0}=\left(\frac{P}{P_0}\right)^{\frac{\gamma-1}{\gamma}}=\frac{P}{P_1}$$

whence

$$P_1=P^{\frac{1}{\gamma}}\ P_0^{\frac{\gamma-1}{\gamma}}\,.$$

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[1] Rayleigh, Sound, Vol. II, second edition, p. 22.

If the pressure is not quite P but P′ the instantaneous temperature on adiabatic expansion would be

$$T' = T_0 \left(\frac{P'}{P_0} \right)^{\frac{\gamma-1}{\gamma}}$$

and if P'_1 is the final pressure observed we have in addition

$$P'_1 = P' \left(\frac{T_0}{T'} \right)$$

$$\therefore \quad P'_1 = (P')^{\frac{1}{\gamma}}, \; (P_0)^{\frac{\gamma-1}{\gamma}}$$

Comparing the value for P'_1 with that for P_1 it is plain that if $P' > P$ then $P'_1 > P_1$.

And since it is generally assumed that the equalisation of pressure is instantaneous, to close the stop-cock too soon would render the final pressure higher than if it were closed at the right instant. Thus under the circumstances

$$\frac{\text{Log } P_0 - \text{Log } P}{\text{Log } P_0 - \text{Log } P'_1} > \text{true value for } \gamma.$$

If on the other hand, this interval be overshot, the final pressure tends more and more towards P, owing partly to the surging of the outside air and partly to the radiation effects, so that in the two extreme cases the fraction (1) might take any value between infinity when P_1 tends to P_0 and unity when P_1 tends to P.

In a form of apparatus we have here, the carboy has a capacity of 47·5 litres and is provided with a stoppered neck of diameter about 4·6 cms. On first trials the generality of students have been consistently getting a value of about 1·35—1·37 for the ratio of specific heats though under identical laboratory conditions carboys provided with narrower mouths give very nearly the correct value, namely, 1·40. It is indeed this discrepancy that has provoked the present investigation. The authors, therefore, propose to calculate the time necessary for equalisation of pressure, for different diameters of the aperture and for a given pressure difference and verify their results by experiments. Since the efflux takes place through appreciably large orifices the viscosity factor is left out of consideration.

Equation for the time.

Let the pressure of air within the carboy initially be P_0 when communication is set up with the surrounding air, let the pressure be P' after a time t sec., so that when $t=0$, $P'=P_0$.

Let P be the pressure of the surrounding atmosphere.

Let ρ_0 be the density of air within the carboy when the pressure is P_0. ρ' the density after time t sec., so that when $t=0$, $\rho'=\rho_0$ and ρ the density finally, that is, when equalisation of pressure is attained. It is evident that since the expansion is adiabatic the final density ρ at the instant of equalisation is different from that of the surrounding atmosphere, though the pressures are equal.

Let the volume of the carboy be L; mass of air initially is $L\rho_0$ and that finally $L\rho$, mass of air in the carboy at time t is $L\rho'$, therefore, mass of air escaping in time t is $L(\rho_0-\rho')$.

Rate of loss is

$$\frac{d}{dt}L(\rho_0-\rho')=-L\frac{d\rho'}{dt} \text{ since } \rho_0 \text{ constant.}$$

It is shown in books on Hydrodynamics[1] that the rate of discharge of mass

$$=c\mathrm{A}\sqrt{\frac{2\gamma\rho'\mathrm{P}'}{\gamma-1}}\sqrt{\left\{1-\left(\frac{\mathrm{P}}{\mathrm{P}'}\right)^{\frac{\gamma-1}{\gamma}}\right\}\left(\frac{\mathrm{P}}{\mathrm{P}'}\right)^{\frac{2}{\gamma}}}$$

where A is the area of orifice and e the co-efficient of contraction of the vein. In the present experiment the pressure difference, being about 3 cms. of mercury, as will be seen from the numerical data, is well within the range for which this equation is valid.

In adiabatic changes

$$\frac{\mathrm{P}}{\mathrm{P}'}=\left(\frac{\rho}{\rho}\right)^{\gamma}$$

such that

$$\rho'=\mathrm{P}\left(\frac{\rho'}{\rho}\right)^{\gamma}$$

$$\therefore -\mathrm{L}.\frac{d\rho'}{dt}=c\mathrm{A}\sqrt{\frac{2\gamma(\rho')^{\gamma+1}}{\gamma-1}.\frac{\mathrm{P}}{\rho^{\gamma}}.}\sqrt{\left\{1-\left(\frac{\rho}{\rho'}\right)^{\gamma-1}\left(\frac{\rho}{\rho}\right)^{2}\right.}$$

This on simplification can be put in the convenient form

$$\frac{d\rho'}{\sqrt{(\rho')^{\gamma-1}-(\rho)^{\gamma-1}}}=-\frac{c\mathrm{A}}{\mathrm{L}}\sqrt{\frac{2\gamma}{\gamma-1}.\frac{\mathrm{P}}{\rho^{\gamma}}}.\rho\,dt$$

$$\therefore\int_{\rho^{0}}^{\rho}\frac{d\rho'}{\sqrt{(\rho')^{\gamma-1}-(\rho)^{\gamma-1}}}=-\frac{c\mathrm{A}}{\mathrm{L}}\sqrt{\frac{2\gamma}{\gamma-1}.\frac{\mathrm{P}}{\rho^{\gamma}}}.\rho t.$$

Instead of seeking for a general solution of the integral to the left the problem is rendered simpler by substituting the numerical value 1·40 for γ.[2]

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[1] Lamb, 4th edition, p. 25.

[2] *Cf.* Lummer and Pringsheim 1·4025 : Ann. d. Phys. 1898.
Sh. Shields 1·4029 : Phy. Rev. 1917. Partington 1·4034 : P.R.S. 1921.
K. Koch 1·4055 : Ann. d. Phys. 1908. Brinkworth 1·4032 : P.R.S. 1925.

Then $$\int_{\rho o}^{\rho} \frac{d\rho'}{\sqrt{(\rho')^{\frac{2}{5}}-(\rho)^{\frac{2}{5}}}} = \int_{\rho o}^{\rho} \frac{d\rho'}{\rho^{\frac{1}{5}}\sqrt{\left(\frac{\rho'}{\rho}\right)^{\frac{2}{5}}-1}}.$$

Put $\left(\frac{\rho'}{\rho}\right)^{\frac{1}{5}}=\cosh\theta$ and $\left(\frac{\rho o}{\rho}\right)^{\frac{1}{5}}=\cosh a$.

The given integral is equal to:

$$\int_{a}^{0} 5\rho^{\frac{4}{5}}\cosh^4\theta.d\theta = -\int_{0}^{\infty} 5\rho^{\frac{4}{5}}\cosh^4\theta d\theta.$$

But $$\cosh^4\theta = \left(\frac{e\theta+e-\theta}{2}\right)^4$$

$$=\tfrac{1}{8}[\cosh 4\theta+4\cosh 2\theta+6]$$

Thus finally

$$\int_{\rho o}^{\rho} \frac{d\rho'}{\sqrt{(\rho')^{\frac{2}{5}}-(\rho)^{\frac{2}{5}}}} = -\tfrac{1}{8}\int_{0}^{a} 5\rho^{\frac{4}{5}}\{\cosh 4\theta+4\cosh 2\theta+6\}d\theta$$

$$=\tfrac{5}{8}.\rho^{\frac{4}{5}}\{\tfrac{1}{4}\sinh 4a+2\sinh 2a+6a\}$$

Hence $\tfrac{5}{8}\rho^{\frac{4}{5}}\{\tfrac{1}{4}\sinh 4a+2\sinh 2a+6a\} = \frac{cA}{L}\sqrt{\frac{2\gamma}{\gamma-1}\cdot\frac{P}{\rho^{\gamma}}}.pt.$

$$\therefore \quad t = \frac{\tfrac{5}{8}\rho^{\frac{1}{2}}\{\tfrac{1}{4}\sinh 4a+2\sinh 2a+6a\}}{\frac{cA}{L}\cdot\sqrt{\frac{2\gamma}{\gamma-1}.P}}$$

where of course $a=\cosh^{-1}\left(\frac{\rho o}{\rho}\right)^{\frac{1}{5}}$

The time for equalisation of pressure is thus found in terms of known quantities :

$$cA,\ L,\ \rho,\ \rho_0,\ \gamma \text{ and } P.$$

Experiment and Verification.

If the stop-cock be closed at the right instant the value of the expression

$$\frac{\text{Log } P_0 - \text{Log } P}{\text{Log } P_0 - \text{Log } P_1{}'}$$

no doubt, gives the correct result for γ. As has been stated already, this value tends to be greater or smaller than 1·40 according as the time for which communication is set up is smaller or greater than the required interval for exact equalisation of pressure. If for a particular aperture this ratio is evaluated for gradually increasing times and the results plotted the curve is of the nature shown below, from which the time for equalisation of pressure can be readily read off, corresponding to $\gamma = 1 \cdot 40$.

On the present occasion the volume of the carboy used is 47·5 litres. It is provided with a neck of diameter 4·6 cms. This is, however, closed with a rubber stopper through which passes a glass tube of the required cross-section. The experiment is conducted in succession with three tubes of diameters 0·685, 0·822 and 1·19 cms. respectively. In all these cases the lengths of the tubes are the same, being about 4 cms. The excess of pressure initially of the compressed air within the carboy is about 40 cms. of oil of density 0·908 grms. per c.c. at laboratory temperature 29°·8C. Each time an experiment is commenced the pressure is maintained at approximately the same value and thus readings are taken under nearly the same pressure conditions

The arrangement of apparatus for this purpose is shown in Fig. 1.

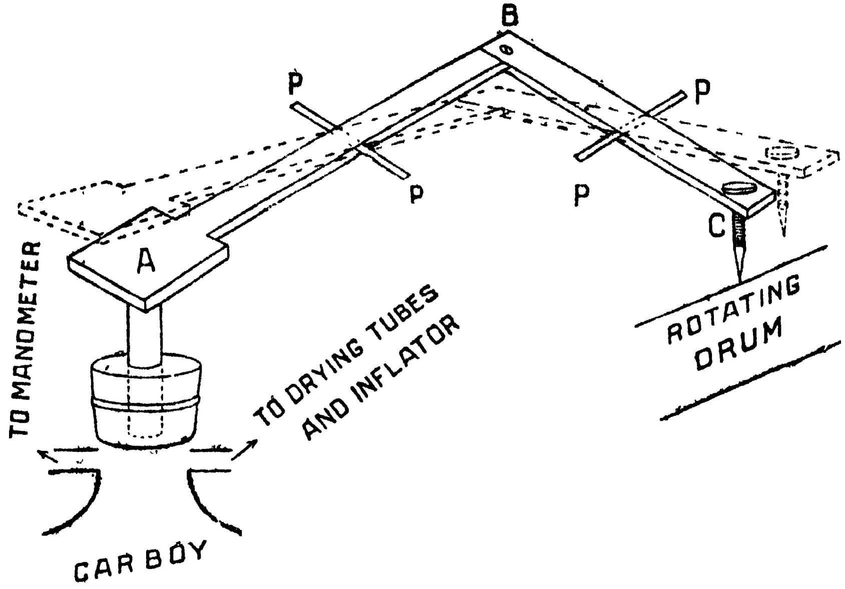

FIG. 1.

AB and BC is a system of two levers hinged at B and each capable of rotating about horizontal axes PP shown in the figure. The lever AB ends in a flat piece the lower surface of which is padded with several folds of good sheet rubber. In its usual position the flat end sits well over the mouth of the glass tube and closes it air-tight so long as it is held there. The free end C of the second lever BC carries a fine light-inked brush just making contact with a rotating drum. The drum has a circumference of 50·54 cms. and is driven at a perfectly uniform rate by a clock-work mechanism. On the present occasion the speed of the drum is adjusted to make one complete rotation in 4·804 sec. as compared with a Dent's standard Astronomical clock beating seconds.

Just before communication is set up with the surrounding atmosphere the drum is set in motion. The instant the end A is lifted off the mouth the brush is also raised when there is a break along the trace. When, however, communication with the surrounding air is cut off by lowering the end A the brush is once again brought into contact with the drum. Thus the length of the gap is proportional to the time interval for which the mouth is kept open. By this arrangement it has been found perfectly possible to keep open the mouth for progressively increasing intervals and measure the times to a high degree of accuracy. The values so obtained are tabulated below :—

TABLE No. I.

Barometer reading (P) = 74·45 cms.

Density of manometric oil 0·908 grms. per c.c. } at 29°·80.
Density of mercury ... 13·53 " " " } at 29°·80.

Diam. of mouth.	Time in Sec.	h_1 cms. of oil.	h_2 cms. of oil.	$\gamma = \frac{\text{Log P}_0 - \text{Log P.}}{\text{Log P}_0 - \text{Log P}'_1}$
0·685 cms. ...	0·2091	41·5	34·1	5·679
	0·2946	48·0	34·35	3·519
	0·4992	39·5	22·60	2·338
	0·7521	37·2	16·85	1·833
	1·3500	39·4	10·70	1·373
	1·5210	38·5	9·70	1·333
0·822 " ...	0·3042	42·2	26·2	2·729
	0·3991	38·4	19·4	2·027
	0·8652	40·0	11·3	1·400
	1·2646	42·0	11·1	1·344
	1·6255	41·1	10·3	1·328
1·190 " ...	0·1484	39·6	18·1	1·831
	0·3041	41·4	13·1	1·472
	0·5989	40·4	10·7	1·359
	0·6750	40·8	10·6	1·342
	1·3500	39·5	9·9	1·333

These values are plotted, times along x-axis and

$$\frac{\text{Log P}_0 - \text{Log P}}{\text{Log P}_0 - \text{Log P}_1'}$$

along the y-axis. From these curves the times for exact equalisation of pressure, *i.e.*, corresponding to $\gamma = 1{\cdot}40$ are found to be 1·25, 0·86 and 0·41 sec. for aperture diameters 0·685, 0·822 and 1·19 cms., respectively.

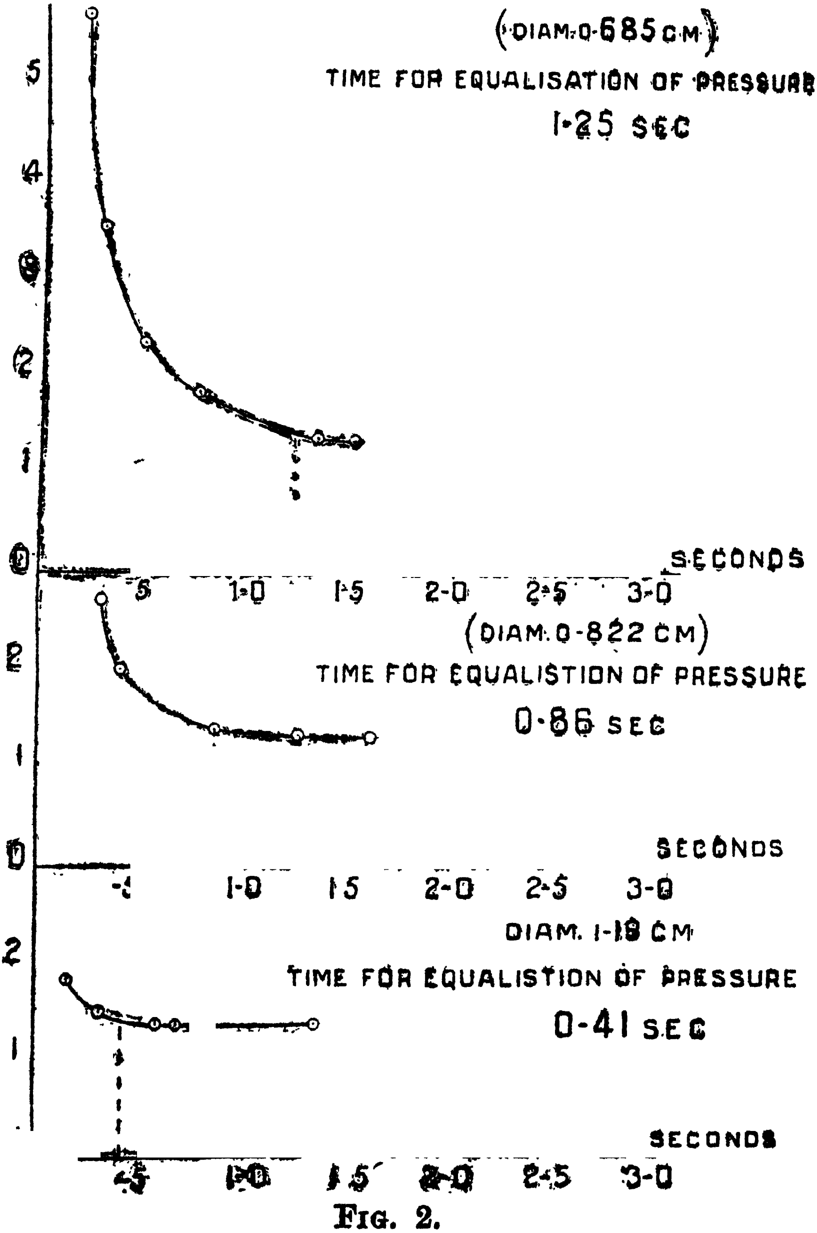

Fig. 2.

Now in the equation for time derived above c for a projecting mouth piece[1] is 1.

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[1] S. Dunkerley's Hydraulics, Vol. I, p. 11.

$$P=74{\cdot}45 \text{ and } P_0=77{\cdot}13 \text{ cms. of mercury ; } L=47{\cdot}5 \text{ litres}$$
$$\rho_0=0{\cdot}001184 \text{ and } \rho=0{\cdot}001154 \text{ grms. per c. c. at } 29^{\circ}{\cdot}8 \text{ C.}$$

$$\therefore \cosh a=\left(\frac{\rho_0}{\rho}\right)^{\frac{1}{2}}=1{\cdot}006, \text{ whence }^{1}\ a=0{\cdot}109.$$

Substituting these values for different apertures we have

TABLE II.

No.	Diam. of aperture.	TIME	
		By calculation.	By experiment.
1	·685 cms.	1·256 sec.	1·25 sec.
2	·822 ,,	·8722 ,,	·86 ,,
3	1·19 ,,	·4162 ,,	·41 ,,
4	4·60 ,,	·0278 ,,	

The agreement between the calculated and experimental values is remarkable indeed.

Radiation Effect.

In so interpolating the curves for $\nu=1{\cdot}40$ it is plain that all radiation effects are neglected. One of the important reasons urged against the use of relatively smaller mouths is that the expansion in such cases may not be truly adiabatic, owing primarily to the radiation from inner walls of the carboy. The following investigation is, therefore, necessary to show the extent of this error.

Now it is known that from the instant the stop-cock is closed there will be gain of heat until a state of equilibrium is set up with that of the surrounding air. For an initial pressure difference of about 40 cms. of oil, the time taken for the final pressure P to become steady is observed to be about 3 minutes. Before, however, this steady pressure is reached a few values of the instantaneous pressures at known

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[1] Byerly's Fourier's Series and Spherical Harmonics, p. 282.

intervals of time are read off and from the known adiabatic equations the instantaneous temperatures are calculated. If ϕ_0 is the temperature difference when the expansion is just complete and ϕ the temperature difference after an interval of t sec., assuming Newton's law of cooling for such small differences as obtain here : ϕ—$\phi_0 e^{-kt}$ substituting values ϕ_1 ϕ_2 ......temp. differences at times t_1, t_2 ..the value of the constant k is found to be 0·00620.

Knowing, therefore, this constant k, the radiation effect can be calculated for any known interval. Thus when the aperture diameter is 0·685 cms. the time for equalisation is found to be 1·25 sec. With the help of the above equation and a knowledge of k, the following tabular form is constructed :—

TABLE III.

Time in sec.	Temperature (Instantaneous).	Temperature excess.	Rate of cooling.
0	29·8	0	0
·1638	29·6	·2	·00124
·5144	29·0	·8	·00496
·7187	28·4	1·4	·00863
·8833	27·9	1·9	·01178
1·0620	27·3	2·5	·01550
1·2500	26·7	3·1	·01922

These readings enable us to find the total " thermometric " radiation correction by the well known graphical method. Accordingly, in Figure 3 the rates of " cooling " $\frac{d\phi}{dt}$ are plotted along y-axis and times along x-axis, so that the area of the curve is equivalent to $\int \frac{d\phi}{dt} dt$. the total radiation during the limits chosen. As will be seen from the graph this amounts to about 0·010 of a degree c which considering the temp. difference can be neglected without serious error.

Thus for such small time intervals as are dealt with, in this paper, radiation effects do not materially influence the result and the times interpolated from the curves in Fig. 2 are fairly accurate.

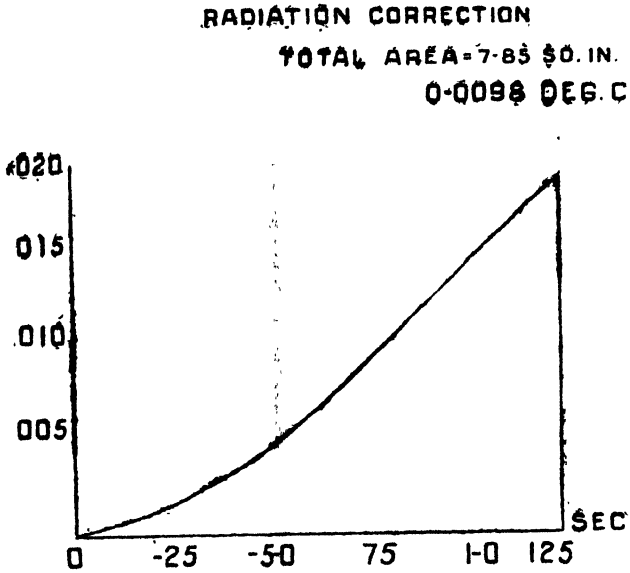

FIG. 3.

Discussion.

Where the determination of the ratio of sp. hts. depends on the measurement of the drop in temp.[1] consequent on adiabatic expansion the diameter of the opening does not materially influence the result, so long as it is appreciably large. Such methods have " the advantage over Clement and Desorme's method that it is unnecessary to close the vessel immediately after making an expansion."[2] If the opening is small the time for equalisation is prolonged and this aggravates the radiation correction which had nevertheless been overcome in the experiments referred to. Where temp. measurements are made it is advantageous to have as large an opening as possible.

Though it is generally held that " any method depending upon a measurement of pressure is not entirely reliable "[3] it has the virtue of being simple and at the same time the readings can be taken under stationary conditions. This feature has recommended its widespread use as a common laboratory experiment. It might seem, as is often suggested, that a wide mouth has several advantages. Though there is instantaneous equalisation of pressure this is followed by the surging in of the outside air, and the result is in consequence lower.

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[1] Walter Makower, Phy. Soc. Proc., Vol. XVIII, pp. 345-358.
H. N. Mercer, Phy. Soc. Proc., Vol. XXVI, pp. 155-165,
H. W. Moody, Phy. Rev., Vol. XXXIV, pp. 275-295.

[2] Mercer, *loc. cit.*

[3] Moody, *loc. cit.*

This fact evidently accounts for the discrepancy mentioned in the opening pages. It is seen from Table II that when the aperture diameter is 4·60 cms. the time for equalisation is as small as 0·0278 sec.—an interval hardly to be manipulated by means of the hand. Whether the mouth be stoppered or provided with a stop-cock it is almost impossible to keep it open for such a small time. It is a matter of common knowledge that a stop-cock can be operated much more quickly than a stopper, the removal and re-insertion of which necessarily entails a longer time. The above investigation seems to favour the view that where the apparatus is designed for pressure measurements no special advantage is gained by making the mouth very wide, as this permits of oscillations being set up and, in consequence, is attended with the surging in of the outside air. Errors arising on this account can be minimised to a large extent by having mouths of suitable diameters which permit of pressure equalisation in manageable intervals without at the same time erring on the other side, that is having too narrow mouths in which case radiation effect becomes sensible.

In conclusion we wish to thank Prof. A. L. Narayan, M.A., D.Sc., F.Inst.P., for his continued interest in this work. We are also much indebted to Prof. S. Purshotham, M.A., of the Mathematics Department for valuable suggestions.

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4

On the Permanent Deformations produced by Contact of Solids.

BY

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1. *Introduction.*

A complete study of the permanent deformations produced by impact of spheres or by application of pressure on spheres placed in contact with slabs of elastic materials having plane faces is interesting from several aspects. A true idea of hardness of materials and the determinations of exact relations amongst the different methods which have been proposed from time to time for measuring this quantity require a thorough knowledge of the nature of the indentations thus produced. It may also be expected to throw some light into the processes by which permanent deformations or cracks are produced when the elastic limits are exceeded. In the present paper an attempt is made towards an investigation of the nature of indentations produced by impact or compression.

2. *Percussion Figures on Glass.*

When a steel ball is allowed to fall on a thick glass slab with plane faces, beautifully regular percussion figures are produced on the glass slab. These were first accurately described by Prof. C. V. Raman.[1] He observed that these cracks begin as circles on the surface and spread inwards into the slab obliquely in the form of a surface of revolution.

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[1] C. V. Raman, Nature, Vol. 104, p. 113, 1919.

Microscopic examinations of about sixty percussion figures produced by the impact of hard steel balls of different diameters falling from different heights on plane faces of thick glass slabs revealed that the circular cracks at the surface are sharp for impacts with relative velocities not much greater than the minimum required for producing cracks. But for greater velocities, this line thickened so that the crack on the surface was not a line but an annular area bounded by two concentric circles and presenting a rugged appearance, the glass on the surface within this area being broken in all possible ways. The penetrations of the cracks into the interior of the glass slabs were found to be in general greater, the greater the amount of compression which produced them. But there was no regularity in the extent of spreading, for even greater compressions sometimes produced less penetration, while different cracks produced by the same ball falling from the same height spread to different extents. The nature of the surfaces formed by the cracks in the interior, however, were always the same. These facts show that cracks in the interior are due to exceeding the shear limits, for as has been shown by A. Mallock,[2] shear ruptures are very clean and sharp and spread in definite directions to apparently arbitrary extents. The cracks on the surface are shear ruptures for small velocities of impact. The irregular breaking for larger velocities of impact shows that the cracks are volume ruptures. The range between the minimum velocity to produce a clean crack and that to produce a rough one is fairly big and hence it may be concluded that the volume limit for rupture is much greater than the distortion limit.

The tables below give the results of microscopic measurements of the inner and outer diameters of these annular areas.

[2] A. Mallock, Proc. Roy. Soc., A., 82, p.

In the first column are given the heights from which the balls were allowed to fall. The second and the third columns give the inner and outer diameters of the cracks on the surface. The fourth column gives the diameters of the circles of contact calculated from Hertz's theory[3] of impact of elastic bodies, which gives the diameter

$$d=2r^{\frac{2}{5}}\left[\frac{15\pi v^2}{16}(\mathrm{D}_1+\mathrm{D}_2)m\right]^{\frac{1}{5}}$$

where the velocity of impact is v, the mass and radius of the steel ball are m and r respectively, those of the glass slab being taken to be infinitely large. D_1 and D_2 represent the quantities

$$\frac{3k_1+4\mu_1}{4\pi\mu_1(3k_1+\mu_1)} \quad \text{and} \quad \frac{3k_2+4\mu_2}{4\pi\mu_2(3k_2+\mu_2)}$$

where k_1 and k_2 are the volume elasticities and μ_1 and μ_2 the rigidities of glass and steel respectively within the elastic limits. On further simplification we have,

$$l=r\left\{20\pi\rho hg\left[\frac{3k_1+4\mu_1}{\mu_1(3k_1+\mu_1)}+\frac{3k_2+4\mu_2}{\mu_2(3k_2+\mu_2)}\right]^{\frac{1}{5}}\right\}$$

where g is the acceleration due to gravity, ρ the density of the steel sphere, and h the height from which it falls.

The percussion figures were also studied by an interference method. For these experiments the percussion figures were produced on good optical surfaces (the plane face of a large broken condensing lens) and interference fringes were produced between this and a glass plate having a good optically plane surface. The fringes inside the circular area of contact were found to be as straight as those outside, thus showing that the surface of the glass within the circular area of contact remains plane even after the impact. The distances between consecutive lines inside two of the percussion figures examined were respectively 0·01013 cm. and 0·01020 cm., while distance between consecutive lines at a region sufficiently removed outside the percussion figure was 0·01011 cm. This shows that the surface within the region of impact remains parallel to the original surface. The depression of this surface below its original level was measured by the displacement of an interference line inside the percussion figure with reference to those at a great distance outside. This depression is given in the fifth column. The sixth column gives the elastic depression as calculated theoretically from Hertz's theory. This is obtained from the relation

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[3] Hertz, Miscellaneous Papers, translated by Jones and Schott, pp. 147-162.

$$\delta=r\left\{\frac{5\pi\rho gh}{2}\cdot\frac{3k_1+4\mu_1}{\mu_1(3k_1+\mu_1)}\right\}^{\frac{2}{5}}$$

Tables I, II and III give respectively the results for percussion figures produced by steel balls of diameters 2·54, 2·05 and 1·78 cms. All the measurements are in centimetres.

TABLE I.

(*Ball diameter* = 2·54 cm.)

Height of fall.	Internal diameters of cracks.	External diameters.	Theoretical diameter of contact area.	Permanent depression of central parts.	Elastic depression.
10·49	0·169	0·169	0·1672		
18·80	0·167	0·184	0·1810		
20·75	0·169	0·197	0·1916		
25·78	0·187	0·195	0·2002		
28·83	0·193	0·208	0·2046		
32·26	0·181	0·208	0·2093		
35·97	0·208	0·215	0·2139		
38·99	0·162	0·218	0·2174		

TABLE I—*contd.*

Height of fall.	Internal diameter of cracks.	External diameter of cracks.	Theoretical diameter of contact area.	Permanent depression of central parts.	Elastic depression.
42·82	0·151	0·222	0·2216		
46·66	0·146	0·228	0·2259		
22·61	0·191	0·191	0·195	$0·224 \times 10^{-5}$	$5·54 \times 10^{-3}$
31·75	0·193	0·195	0·2087	$0·831 \times 10^{-5}$	$6·35 \times 10^{-3}$
38·48	0·200	0·205	0·2132	$1·60 \times 10^{-5}$	$6·86 \times 10^{-3}$
48·01	0·201	0·209	0·2278	$2·36 \times 10^{-5}$	$7·49 \times 10^{-3}$

TABLE II.

(*Ball diameter = 2·05 cm.*)

Height of fall.	Internal diameter of cracks.	External diameter of cracks.	Theoretical diameter of contact area.	Permanent depression of central area.	Elastic depression.
13·78	0·151	0·155	0·1448		
20·17	0·133	0·162	0·1563		
26·57	0·131	0·181	0·1651		
32·21	0·135	0·166	0·1712		
35·94	0·142	0·183	0·1757		
40·00	0·155	0·178	0·1793		
43·71	0·161	0·182	0·1824		
47·55	0·162	0·180	0·1856		
51·16	0·166	0·185	0·1882		
55·14	0·168	0·198	0·1911		
37·97	0·176	0·176	0·1775	$0·36 \times 10^{-5}$	$5·50 \times 10^{-3}$
47·75	0·178	0·181	0·1859	$0·58 \times 10^{-5}$	$6·03 \times 10^{-3}$
66·80	0·190	0·201	0·2011	$1·17 \times 10^{-5}$	$7·06 \times 10^{-3}$
76·58	0·191	0·203	0·2042	$1·75 \times 10^{-5}$	$7·29 \times 10^{-3}$
84·58	0·196	0·205	0·2107	$2·75 \times 10^{-5}$	$7·58 \times 10^{-3}$

TABLE III.

(*Ball diameter* = 1·78 cm.)

Height of fall.	Internal diameter of crack.	External diameter of crack.	Diameter of contact-area.
15·49	0·124	0·125	0·1247
19·76	0·133	0·133	0·1309
22·86	0·130	0·136	0·1348
26·21	0·124	0·140	0·1386
29·16	0·128	0·143	0·1416
32·44	0·131	0·147	0·1445
37·61	0·142	0·150	0·1488
43·33	0·143	0·155	0·1532
49·02	0·146	0·159	0·1570
55·30	0·145	0·165	0·1609

From the above results it can be seen that the external diameters of the cracks are nearly equal to the diameters of the circles of contact while the internal ones are smaller. S. K. Banerji[4] has shown that the cracks produced occur at the circle bounding the area of contact of the two bodies. Hence these results show that the breaking begins much earlier than when the maximum compression is attained and also that the elastic constants of glass do not change appreciably when the pressures are applied and released with the rapidity of the dropping balls.

The nature of the elevation of the part just outside the crack was studied by the interference method. It is seen

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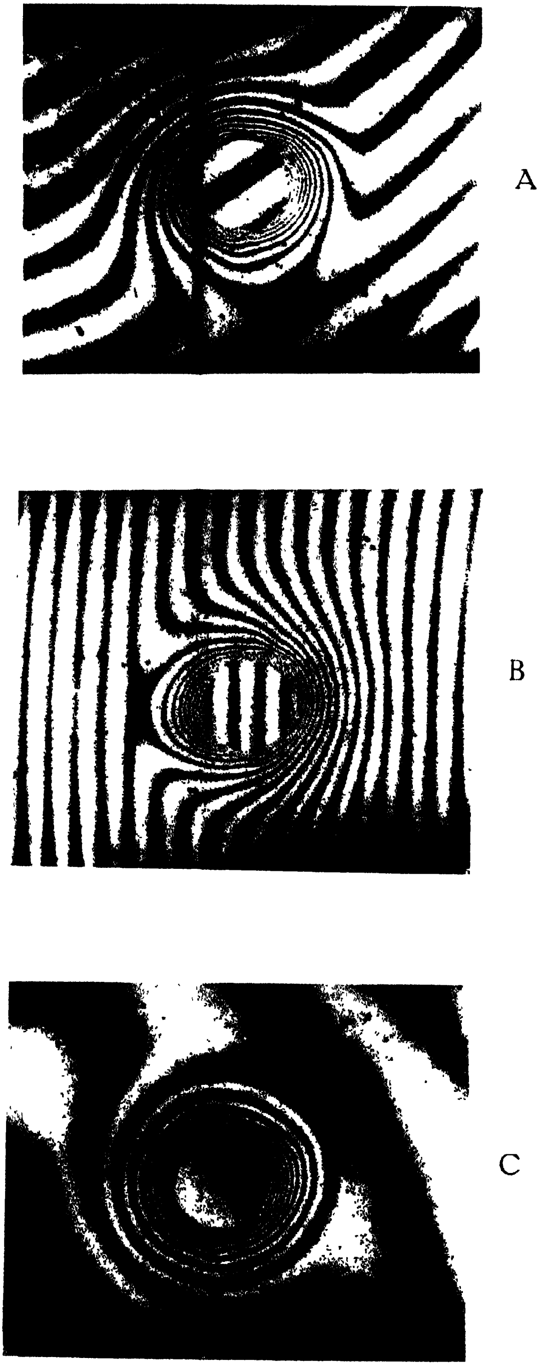
[4] Bulletin of the Calcutta Mathematical Society, Vol. XII, 1921, pp. 93-96. See also S. Fuchs, Phys. Zeit., 1913.



Percussion figures on glass.

from the photographs (plate), that the elevation of the external part is much greater than the depression of the central portion. This does not, however, indicate any change of density, for the cracks which extend into the interior of the glass slab have a finite volume. This is evident from the interference rings that are produced round the percussion figures either by transmitted or reflected light directly from the glass slab without using any auxiliary glass plate as is illustrated by the photographs in C. V. Raman's paper.[5] It is indeed probable that no real change of density occurs but owing to the irregular fractures which accompany the percussion figure, this is not easy to demonstrate conclusively.

3. *Static Compression-Figures in Glass.*

The effects of static pressures on steel balls in contact with glass slabs were also similarly studied. The pressures were applied very slowly by means of a lever and a sliding weight. In order to slow down the application of pressure, the lever was held in the hand and gradually lowered. The general nature of the results were similar to the dynamic experiments. The results are given in Tables IV, V and VI for the three balls of diameters 1·428, 1·585 and 2·223 cms., respectively. The first column gives the total pressure, the second and the third columns give respectively the internal and external diameters of the circular cracks, the fourth column, the diameters of the circles of contact as calculated from Hertz's theory according to the equation

$$d=2\left\{\frac{3\pi r}{4}(D_1+D_2)P\right\}^{\frac{1}{3}}$$

where P is the total pressure.

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[5] *Ibid.*

TABLE IV.

(*Ball diameter*=1·428 cms.)

Pressure in dynes.	Internal diam. of the cracks.	External diam. of the cracks.	Diameters of the circles of contact.
$12·27 \times 10^7$	0·088	0·103	0·0940
$10·86 \times 10^7$	0·087	0·099	0·0902
$9·29 \times 10^7$	0·085	0·092	0·0856
$7·63 \times 10^7$	0·083	0·085	0·0808
$6·50 \times 10^7$	0·080	0·080	0·0760

TABLE V.

(*Ball diameter*=1·585 cms.)

Pressure in dynes.	Internal diam. of the cracks.	External diam. of the cracks.	Diameters of the circles of contact.
$11·59 \times 10^7$	0·085	0·104	0·0954
$10·40 \times 10^7$	0·082	0·097	0·0921
$9·86 \times 10^7$	0·084	0·092	0·0889
$7·82 \times 10^7$	0·086	0·086	0·0836
$6·50 \times 10^7$	0·080	0·080	0·0789

TABLE VI.

(*Ball diameter*=2·223 cms.)

Pressure in dynes.	Internal diam. of the cracks.	External diam. of the cracks.	Diameters of the circles of contact.
$12·27 \times 10^7$	0·098	0·126	0·1089
$10·86 \times 10^7$	0·100	0·117	0·8022
$9·29 \times 10^7$	0·097	0·111	0·0992
$7·63 \times 10^7$	0·095	0·098	0·0929
$6·50 \times 10^7$	0·094	0·096	0·0881

For the static experiments the external diameters of the impressions are found from the above results to be greater than the maximum diameters of the circles of contact, taking for elastic constants the values for small deformations. In this respect, the results for the static experiments differ from those for the effects of dynamic impacts.

4. *Impact on Steel Blocks.*

The general nature of the indentations produced on the plane face of a soft cast steel block by dropping hard steel balls was found to be that the spot where the impact occurred was depressed forming a cup while the sides were raised up. These were studied by an optical lever. The apparatus consists of a triangular brass strip one of the sides being much smaller than either of the others which are equal. The strip stands on three pointed legs one at each corner. A small plane mirror was fixed at the angular point opposite the smallest side of the triangle. The tilting of the mirror as this angular point moves along the indentation is observed by a telescope and scale. The nature of the deformations is indicated by a graphical representation of the results.

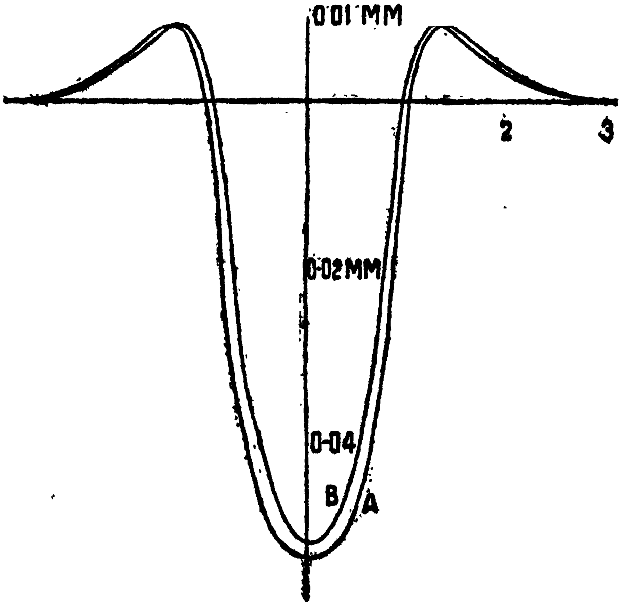

FIG. 1.

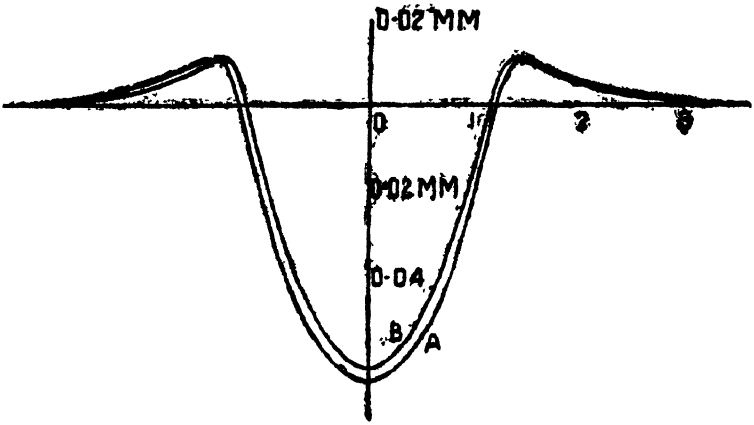

FIG. 2.

Figs. 1 and 2 represent two of these curves in which the abscissae and the ordinates are plotted on different scales. Curve (A) in each figure is obtained from readings taken immediately after and (B) from readings taken a day or two after the production of the impressions. Volumes of the depressed and elevated portions, radii of curvature of the central part and the diameters of the depressions are calculated from the figures and given below.

Descriptions of the Graphs.

Fig. 1.

Radius of the steel ball ...	8·74 mm.
Height of fall ...	126·50 cm.

Curve (A)

Diameter of the depressed area ...	2·02 mm.
Volume of depression ...	$9{\cdot}66 \times 10^{-2}$ mm.^{3}
Volume of elevation ...	$7{\cdot}68 \times 10^{-2}$ mm.^{3}
Radius of curvature ...	9·58 mm.

Curve (B)

Diameter of the depressed area	1·94 mm.
Volume of depression	$7{\cdot}86 \times 10^{-2}$ mm.^{3}
Volume of elevation	$8{\cdot}08 \times 10^{-2}$ mm.^{3}
Radius of curvature	9·15 mm.

Fig. 2.

Radius of steel ball	11·12 mm.
Height of fall	94·85 cm.

Curve (A)

Diameter of the depressed area	2·42 mm.
Volume of depression	$12{\cdot}12 \times 10^{-2}$ mm.^{3}
Volume of elevation	$8{\cdot}36 \times 10^{-2}$ mm.^{3}
Radius of curvature	12·86 mm.

Curve (B)

Diameter of the depressed area	2·30 mm.
Volume of depression	$9{\cdot}9352 \times 10^{-2}$ mm.^{3}
Volume of elevation	$9{\cdot}0876 \times 10^{-2}$ mm.^{3}
Radius of curvature	12·04 mm.

It will be observed that the volumes of the depressed parts of the deformations are equal to the volumes of elevation of the surrounding portions if sufficient time is allowed to elapse between the impact and the measurements. If the readings, however, are taken immediately after the impact the depressed volume is found in the case of the dynamic experiments to be much greater than the elevated portion. Thus we see that the contraction in volume which occurs during sudden compression takes some time to get removed. The process how the dents are partially filled up can be seen easily from the figures. Thus it is seen that the density of steel is increased by sudden compression beyond the elastic limits, but the change is not permanent, it reverts to the original state after some time.

5. *Static Pressures on Steel Blocks.*

Permanent deformations on steel blocks by application of pressure on hard steel balls placed in contact were similarly studied. The results are illustrated in Figs. 3 and 4.

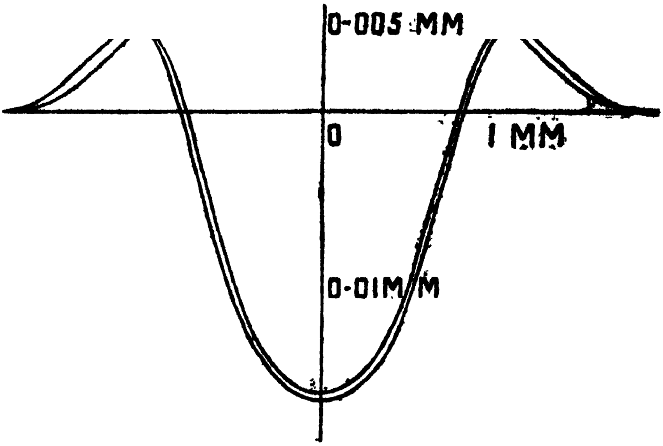

FIG. 3.

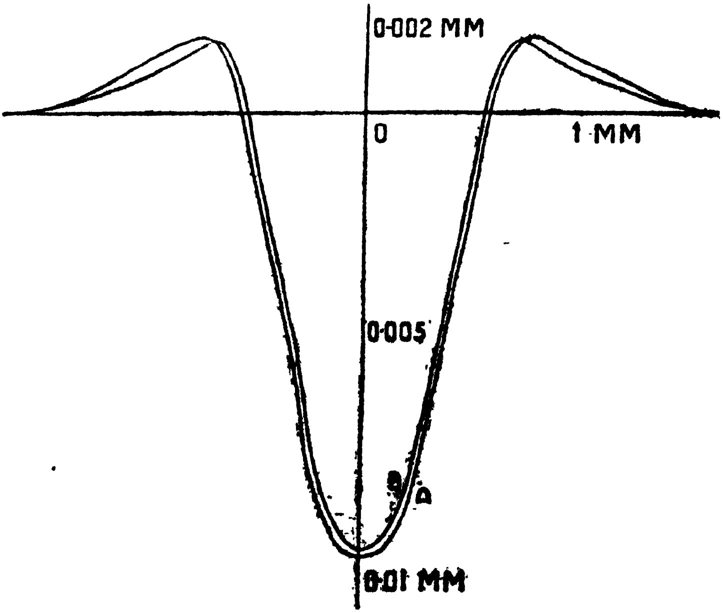

FIG. 4.

Fig. 3.

Radius of the ball	8·74 mm.
Total pressure	$9{\cdot}978 \times 10^7$

Curve (A)

Diameter of depressed area	1·32 mm.
Volume of depression	2·213 × 10^{-2} mm.^{3}
Volume of elevation ...	2·410 × 10^{-2} mm.^{3}
Radius of curvature ...	13·5 mm.

Curve (B)

Diameter of the depressed area	1·29 mm.
Volume of depression ...	2·101 × 10^{-2} mm.^{3}
Volume of elevation ...	2·162 × 10^{-2} mm.^{3}
Radius of curvature ...	13·60 mm.

Fig. 4

Radius of the ball ...	8·74 mm.
Total pressure ...	7·935 × 10^7 dynes

Curve (A)

Diameter of the depressed area	1·16 mm.
Volume of depression ...	0·4608 × 10^{-2} mm.^{3}
Volume of elevation ...	0·545 × 10^{-2} mm.^{3}
Radius of curvature ...	14·2 mm.

Curve (B)

Diameter of the depressed area	1·11 mm.
Volume of depression ...	0·4371 × 10^{-2} mm.^{3}
Volume of elevation ...	0·4539 × 10^{-2} mm.^{3}
Radius of curvature ...	15·0 mm.

For the static experiments, the volume of elevation immediately after the deformation is produced is greater than the volume of depression. This confirms the important results obtained by Lea and Thomas[6] that the density of steel is decreased by static compressions. In this case also the density reverts to the original value after some time.

[6] Lea and W. N. Thomas, Engineering 100, pp. 1-3. July 2, 1915.

The radius of curvature of the depressed part is greater than the radius of the steel ball in either static and dynamic experiments but for static experiments the radii were much greater in proportion to the radii of the steel balls used, than those for the dynamic. Radius of curvature of the dents produced by different velocities of impact and by different static compressions was also measured by an optical method. It was observed that the radii decreased with the increase of velocity of impact or static pressure. The small values of the radii for the dynamic experiments were due to the compressions in the dynamic cases being much greater than those in the static ones. For small velocities of impact, the radii were of the same order as those for the static experiments.

TABLE VII.

Radius of Curvature of the Dents in Dynamic Experiments.
(*Radius of the ball* = 1·112 cm.)

Height of fall.	Radius of curvature.
36·2 cm.	1·522 cm.
50·0 cm.	1·404 cm.
69·5 cm.	1·384 cm.
92·7 cm.	1·338 cm.
126·2 cm.	1·299 cm.

TABLE VIII.

Radius of Curvature of the Dents in the Static Experiments.
(*Radius of the ball* = 0·739 cm.)

Total pressure.	Radius of curvature.
$10{\cdot}53 \times 10^7$ dynes	1·054 cm.
$10{\cdot}21 \times 10^7$ dynes	1·063 cm.
$9{\cdot}60 \times 10^7$ dynes	1·078 cm.
$9{\cdot}02 \times 10^7$ dynes	1·102 cm.
$8{\cdot}20 \times 10^7$ dynes	1·124 cm.

The difference of behaviour of the material under static and dynamic compressions should not, however, be regarded as curious in view of Seehase's[7] conclusions that the stresses for impact tests are different from those for slow compressions.

The elevations at the sides of the cups can be also readily seen by means of interference fringes produced between the steel surface and a glass plate.

6. Criticism of Methods of Hardness Determinations.

The results given in the graphs show that there are certain inaccuracies in the various indentation methods for measuring hardness. In Brinell's method,[8] the diameter of the depressed portion as measured by a microscope is utilised. But the real diameter that should be taken is that of the intersection of the dent with the original surface and not the diameter actually measured by a microscope. It is further inaccurate to take the dent as quite spherical with radius of curvature equal to that of the ball in determining the area of the depressed surface. Calculations from the graphs, however, show that the dents are rather hyperbolical.

The methods in which the depth of the dents are used, have been rightly criticised by Batson,[9] but the figure given by him does not represent the true phenomena, for neither does the dent acquire the same curvature as the uncompressed ball, nor is the edge so sharp, as will be seen from the graphs. The effects of these inaccuracies are of more importance in methods such as that of Martel[10] in which the determinations of the volumes of the dents are required.

Summary.

(*a*) Percussion figures produced by steel balls of different diameters falling from different heights on glass slabs and also those produced by slow pressures on balls in contact with them were accurately studied. The crack spreads into the glass as a clearly defined and very regular surface of revolution, while on the surface it appears as an annular area inside which the glass is broken. The external diameter of the annulus is nearly equal to the diameter of the circle of contact, calculated on Hertz's theory. A small fraction of the depression of the interior remains permanent. The sides are raised to a great extent but this is counterbalanced by the crevices inside at least to some extent.

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[7] Science Abstracts 18A, 1915, Abstract No. 1174, pp. 499-500.

[8] Wahlberg, Journal of the Iron and Steel Institute, 1901, No. 1, p. 243, etc.

T. Turner, Notes on Tests for Hardness, Journal of the Iron & Steel Ins., 79, 1909.

[9] Dictionary of Applied Physics, Vol. I, pp. 191-192: a general survey of all the methods of measuring hardness is also given there.

[10] T. Baker and T. F. Russel—Note on "The Ball Test," Journal of Iron and Steel Institute, 1920. No. 1, Vol. CI.

(*b*) Examinations of the permanent deformations produced by impact of hard steel balls on a soft cast steel block show that the central part is depressed while the sides are raised up. *The volumes of depression are greater than the volume of elevation immediately after the impact, but after some time these two volumes are equalised,* the interior of the cup being raised up to a much greater extent than the elevated portion is lowered. In static compressions on steel, however, the volume of depression is less than the volume of elevation immediately after the deformation is produced. But here in course of time the elevated portion falls down to a greater extent than the central part is raised so that the volumes are again equalized. It is concluded that the density of steel is temporarily increased by impact and decreased by slow compression.

(*c*) The depressed part is not quite spherical. The radius of curvature of the centre is greater than the radius of the ball and increases with decrease of pressure. Some methods of determining hardness used in practice should be modified in view of this for accurate work.

My best thanks are due to Professor C. V. Raman, F.R.S., for suggesting the problem and his valuable criticisms during the progress of the work.

5

On the Impact of an Elastic Hammer on a Pianoforte-String.

BY

PANCHANON DAS, M.SC.

1. *Introduction.*

When an elastic body is subjected to moderate stress, the components of strain produced are proportional to the corresponding components of stress, and the result is known as Hooke's Law. However when two bodies, the bounding surfaces of which are approximately plane, press against each other, the resultant pressure between them has been shown by Hertz to be proportional to the (3/2)th power of the relative compression. As the former law is mathematically much simpler, the problem of the pianoforte was tackled on the basis of Hooke's law in a previous paper by the author.[1] While that was passing through the press, a rough experimental test was carried out in the laboratory of the Indian Association for the Cultivation of Science, to decide which of the two laws was correct in the case of the pianoforte. An ordinary pianoforte hammer, of which the hinged extremity was fixed in a clamp, was mounted on a rigid unyielding block, and loaded by means of a scale-pan suspended from a point on the arm of the hammer, with weights ranging from 100 gm. to 1,500 gm. The corresponding amounts of compression of the felt-covering were measured by means of a travelling microscope by observing the displacement of the sharp point of a pin stuck into the wooden core of the hammer. The curve of load against compression was found to be roughly a straight line passing through the origin, pointing to Hooke's Law. We shall presently see that the range of pressure investigated by us experimentally is sufficient to cover the impulsive pressure that is developed for moderate velocities of impact. If we take the frequency of the C′-note of a pianoforte to be 256, its period is 1/256. Assuming after Helmholtz that the impact lasts for about half this period, duration of impact is seen to be 1/512. The mass of a pianoforte hammer was found to be 6·6 gm. The velocity of the hammer varies from 5 ft. to 60 ft. per second according to Ortmann.[1] If we take it to be 5 ft. or 150 cm. per second, then assuming that the velocity of the hammer is reversed by the impact, the total change of momentum is $2 \times 6{\cdot}6 \times 150$ units. Thus the average pressure during the impact is about 1000 gm. if one plays very softly, and this appears to be within the range of Hooke's Law.

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[1] "On the Pressure exerted by an Elastic Hammer impinging on a Pianoforte-string," Proc. Ind. Assn., Vol. IX, p. 297, 1926.

The ratio which had been denoted by E in the paper cited, of the load to the compression was found from the fore-mentioned graph to be of the order of 10^0. The tension T of pianoforte strings is usually of the order of magnitude of 10^7 to 10^8 dynes. Thus the ratio E/T is rather a small quantity, whereas the approximation occurring in § 1 of the paper cited was based on the assumption that the ratio was a large quantity. The co-efficient occurring in the *exact* expression for pressure as a function of time were also calculated there without any assumption as regards the value of E/T, but only for the first and second epoch, whereas there is good ground for supposing that actually the impact extends well up to the fifth or the sixth epoch. Hence a calculation of these co-efficients up to the fifth epoch has been given the first place in this paper by way of supplementing the previous work.

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[1] Ortmann, On Piano-Touch and Tone.

Kaufmann in his well-known paper[1] has given an approximate treatment of the problem on the assumption, that when the hammer strikes the string very near one end, the part of the string lying between the hammer and the near end (we shall call this the striking-length) remains straight and can therefore be regarded as a rigid line. In § 2 of this paper we extend his result to the case of the elastic hammer. But it will be shown that Kaufmann's formula is a special case of our own formula. A study of the displacement of the string during and after impact, which was left out in the previous work, has been given for the rigid hammer in § 3 and § 4. It was pointed out before, that the equation having the duration of impact for a root cannot in general be solved algebraically. So a graph of duration of impact against striking length has been drawn for a rigid hammer in the concluding article.

§ 1.

Exact Pressure-co-efficients.

A brief outline of the previous results may with advantage be given here. If the striking-length of the string be a, then the motion of the string is best studied by dividing the whole period of impact into a number of epochs each of magnitude $2a/c$, where c is the wave-velocity. If u be the compression of the hammer, the corresponding pressure is Eu, where E is the constant of Elasticity referred to in the Introduction. At any instant t given by $n. 2a < ct < (n+1) 2a$, the compression u is given by

$$u = \frac{2T}{E} \sum_{1}^{n+1} \phi r(ct) \qquad \ldots \quad (1)$$

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[1] Annalen der Physik, Bd. 58, 1896 (p. 678).

where $\phi_{n+1}(Z)=e^{\alpha Z_n}\sum_{0}^{n}{}_{n+1}a_r\, Z_n^r+e^{\beta Z}\sum_{0}^{n}{}_{n+1}b_r\;{}_1Z_n^r$ ... (2)

and $Z=ct$, $Z_r=ct-r.2a$, and α, β are the

roots of the equation

$$x^2+\frac{E}{2T}x+\frac{E}{mc^2}=0, \qquad \text{... (3)}$$

T being the tension, and m the mass of the hammer.

The constants ${}_{n+1}a_r$, ${}_{n+1}b_r$, *etc.* are related to each other by means of the following equations :—

$$(\alpha-\beta).{}_{n+1}a_{r+1}+(r+2).{}_{n+1}a_{r+2}$$

$$=\frac{E}{2T}\left({}_na_{r+1}+\frac{{}_na_r}{r+1}\alpha\right) \qquad \text{... (4)}$$

$$(\beta-\alpha).{}_{n+1}b_{r+1}+(r+2).{}_{n+1}b_{r+2}$$

$$=\frac{E}{2T}\left({}_nb_{r+1}+\frac{{}_nb_r}{r+1}\beta\right) \qquad \text{... (5)}$$

$${}_{n+1}a_0+{}_{n+1}b_0=0 \qquad \text{... (6)}$$

$${}_{n+1}a_0.\alpha+{}_{n+1}a_1+{}_{n+1}b_0.\beta+{}_{n+1}b_1=0 \qquad \text{... (7)}$$

In particular, if we write

$$\lambda=\frac{2T}{E}$$

we have,

$${}_1a_0=-{}_1b_0=\frac{V}{c}\cdot\frac{1}{\lambda(\alpha-\beta)} \qquad \text{... (8)}$$

$${}_2a_0=-{}_2b_0=\frac{V}{c}\cdot\frac{1}{\lambda^2(\alpha-\beta)^2} \qquad \text{. (9)}$$

$$a_1=\frac{V}{c}\cdot\frac{\alpha}{\lambda^3(\alpha-\beta)^2} \quad \ldots \quad (10)$$

$${}_2b_1=\frac{V}{c}\cdot\frac{\beta}{\lambda^3(\alpha-\beta)^2} \quad \ldots \quad (11)$$

V stands for the initial velocity of the hammer.

Co-efficients of higher order than these were not calculated in the previous paper. So we first find out the co-efficients for the third epoch, *viz.*,

$${}_3a_0,\ {}_3a_1,\ {}_3a_2 \text{ and } {}_3b_0,\ {}_3b_1,\ {}_3b_2.$$

If we put $n=2$ in the results (35) and (36) of the previous paper, we get

$${}_3a_2=\frac{V}{c}\cdot\frac{}{\lambda^3(\alpha-\beta)^3}\cdot\underline{|2} \quad \ldots \quad (12)$$

$${}_3a_1=\frac{V}{c}\cdot\frac{1}{|\lambda^4(\alpha-\beta)^4}(1-\beta\lambda) \quad \ldots \quad (13)$$

The corresponding b-co-efficients are obtained by interchanging α and β. Hence putting $n=2$ in (6) and (7), we get after simplification,

$${}_3a_0=\frac{V}{c}\cdot\frac{1}{\lambda^5(\alpha-\beta)^3}\cdot(1+2\alpha\beta\lambda^2) \quad \ldots \quad (14)$$

We next pass on to the fourth epoch. If we put $n=3$ in the results (35) and (37) of the previous paper, we get

$${}_4a_3=\frac{}{c}\cdot\frac{}{\lambda^4(\alpha-\beta)^4}\cdot\frac{}{\underline{|2}} \quad \ldots \quad (15)$$

$${}_4a_2=-\frac{V}{c}\cdot\frac{1}{\lambda^5(\alpha-\beta)^5}\cdot\frac{\alpha+3\beta}{\alpha-} \quad \ldots \quad (16)$$

To get ${}_4a_1$, we put $n=3$ and $r=0$ in (4), Thus,

$$(\alpha-\beta)\cdot{}_4a_1+2\cdot{}_4a_2=\frac{1}{\lambda}\cdot{}_3a_1+\frac{{}_3a_0}{\lambda}\cdot\alpha,$$

which easily gives,

$${}_4a_1=\frac{V}{c}\cdot\frac{(\alpha^2+6\alpha\beta+3\beta^2)\alpha}{\lambda^6(\alpha-\beta)^6} \quad \ldots \quad (17)$$

And from (6) and (7), where we put $n=3$, we get

$${}_4a_0=\frac{\ }{c}\cdot\frac{\ }{\lambda^7(\alpha-\beta)^7}\cdot\frac{\alpha^2+\beta^2+5\alpha\beta}{\alpha^2+\beta^2+2\alpha\beta} \quad \ldots \quad (18)$$

Finally, we deal with the fifth epoch.

Putting $n=4$ in the results (35) and (37) of the previous paper, we get

$${}_5a_4=\frac{V}{c}\cdot\frac{1}{\lambda^5(\alpha-\beta)^5}\cdot\frac{\alpha^4}{\lfloor 4} \quad \ldots \quad (19)$$

$${}_5a_3=\frac{V}{c}\cdot\frac{1-3\beta\lambda}{\lambda^5(\alpha-\beta)^5}\cdot\frac{\alpha^3}{\lfloor 3} \quad \ldots \quad (20)$$

Next, put $n=4$ and $r=1$ in (4) and (5). Thus,

$$(\alpha-\beta)\cdot{}_5a_2+3\cdot{}_5a_3=\frac{1}{\lambda}\cdot{}_4a_2+\frac{{}_4a_1}{2}\cdot\frac{\alpha}{\lambda},$$

whence we get

$${}_5a_2=-\frac{V}{c}\cdot\frac{\alpha^4+8\alpha\beta+6\beta^2}{\lambda^6(\alpha-\beta)^6(\alpha^2-\beta^2)}\cdot\frac{\alpha^2}{\lfloor 2} \quad \ldots \quad (21)$$

Again, put $n=4$ and $r=0$ in (4) and (5). Thus,

$$(\alpha-\beta)\cdot{}_5a_1+2\cdot{}_5a_2=\frac{1}{\lambda}\cdot{}_4a_1+{}_4a_0\cdot\frac{\alpha}{\lambda},$$

whence we get,

$$ {}_3a_1=\frac{V}{c}\,\frac{\alpha^3+12\alpha^2\beta+18\alpha\beta^2+4\beta^3}{\lambda^6(\alpha-\beta)^7(\alpha^2-\beta^2)}.\alpha \qquad \ldots \quad (22)$$

Lastly, put $n=4$ in (6) and (7,. We get, after some reduction,

$$ {}_4a_0=-\frac{V}{c}\,\frac{\alpha^4+16\alpha^3\beta+36\alpha^2\beta^2+16\alpha\beta^3+\beta^4}{\lambda^8(\alpha-\beta)^9(\alpha^2-\beta^2)} \qquad \ldots \quad (23)$$

It may be mentioned once more, that the corresponding b-co-efficients are derived by interchanging α and β.

A numerical study of these will be made in a later paper.

§ 2

String struck near End.

When the striking-length of the string is very short, Kaufmann assumes that this part of the string remains practically straight during the impact and can be regarded as a rigid line. As it turns about the fixed extremity under the pressure of the hammer, its inertia offers a resistance to the motion of the hammer, and Kaufmann takes this resistance into account by attaching to the string at the striking-point, a particle of such mass that its moment of inertia about the fixed end is the same as that of the striking-length of the string. As in the previous paper, we denote the striking-length by a, and the line-density by ρ. Then Kaufmann has shown that the mass of the equivalent particle is $\frac{1}{3}\rho a$.

Let c be the wave-velocity and y_0, y_1, y_2 the displacements of the string for $x=o$, $x<o$, and $x>o$, respectively. Then the equation of motion of the string is

$$\frac{\partial^2 y}{\partial t^2}=c^2\frac{\partial^2 y}{\partial x^2} \qquad \ldots \quad (24)$$

If the displacement of the rigid core of the hammer be ζ, and the compression be u, the equation of motion of the hammer (mass $= m$) is,

$$m\frac{d^2\zeta}{dt^2} = \text{pressure of impact} = -\mathrm{E}u.$$

But $\zeta = y_0 + u$; therefore,

$$m\frac{d^2y_0}{dt^2} + m\frac{d^2u}{dt^2} = -\mathrm{E}u \qquad \dots \quad (25)$$

Now this pressure is resisted (1) by the resolved parts of the tension T of the string, (2) by the inertia of the equivalent particle. Thus

$$\mathrm{E}u = \mathrm{T}\left(\frac{\partial y_1}{\partial x} - \frac{\partial y_0}{\partial x}\right)_{x=0} + \tfrac{1}{3}\rho a.\frac{d^2y_0}{dt^2} \qquad \dots \quad (26)$$

To solve these, we first write down the functional solutions of the equation (24) in the form :—

$$\left.\begin{aligned} y_1 &= f(ct+x) \\ y_0 &= f(ct) \end{aligned}\right\} \qquad \dots \quad (27)$$

Since the part of the string, of which the displacement is y_2, is regarded as straight, its equation is

$$y_2 = \frac{y_0}{a}(a-x) \qquad \dots \quad (28)$$

Substituting (27) and (28) in (26), we get

$$\begin{aligned} \mathrm{E}u &= \mathrm{T}\left\{\frac{y_0}{a} + f'(ct)\right\} + \rho\frac{a}{3}.\frac{d^2y_0}{dt^2} \\ &= \mathrm{T}\left\{f'(ct) + \frac{1}{a}f(ct)\right\} + \frac{\rho a c^2}{3}.f''(ct) \end{aligned} \qquad \dots \quad (29)$$

Substituting this in (25) we get after some simplification

$$\frac{a}{3}f^{\mathrm{IV}}(ct)+f'''(ct)+\left(\frac{\mathrm{E}}{\mathrm{T}}+\frac{1}{a}+\frac{\rho a}{3m}\cdot\frac{\mathrm{E}}{\mathrm{T}}\right)f''(ct)$$

$$+\frac{\rho}{m}\cdot\frac{\mathrm{E}}{\mathrm{T}}f'(ct)+\frac{\rho}{m}\cdot\frac{\mathrm{E}}{a\mathrm{T}}f(ct)=0 \qquad \ldots \quad (30)$$

This is a linear differential equation of the fourth order with constant co-efficients and its solution is of the form

$$f(ct)=\mathrm{A}.e^{p_1ct}+\mathrm{B}.e^{p_2ct}+\mathrm{C}.e^{p_3ct}+\mathrm{D}.e^{p_4ct} \qquad \ldots \quad (31)$$

where A, B, C, D are constants of integration and p_1, p_2, p_3, p_4 are roots of the equation

$$\frac{a}{3}x^4+x^3+\left(\frac{\mathrm{E}}{\mathrm{T}}+\frac{1}{a}+\frac{\rho a}{3m}\cdot\frac{\mathrm{E}}{\mathrm{T}}\right)x^2+\frac{\rho}{m}\cdot\frac{\mathrm{E}}{\mathrm{T}}\left(x+\frac{1}{a}\right)=0 \qquad \ldots \quad (32)$$

Although this biquadratic equation can be solved algebraically, yet such a general solution is too cumbrous for practical purposes. An approximate solution can however be easily obtained, if we note that generally ρ/m is a small quantity of order 0·01. Hence, in order to obtain those roots which are finite, we neglect terms involving ρ/m and get

$$\frac{a}{3}x^2+x+\frac{\mathrm{E}}{\mathrm{T}}+\frac{1}{a}=0 \qquad \ldots \quad (33)$$

The roots of this equation are

$$-\frac{3}{a}\pm\sqrt{\frac{3}{a}}\sqrt{2-\frac{\mathrm{E}a}{\mathrm{T}}} \qquad \ldots \quad (34)$$

As the absolute term in (32) is a small quantity because of the factor ρ/m, there is at least one small root of the equation (32); if this root is an infinitesimal of the first order, the term involving x is one of second order, and the term

involving x^2 is also of second order, and the rest are of still higher orders. Hence these small roots are given by

$$\left(\frac{E}{T}+\frac{1}{a}\right)x^2+\frac{\rho}{m}\cdot\frac{E}{T}\left(x+\frac{1}{a}\right)=0 \qquad \ldots \quad (35)$$

This is a quadratic equation and can be easily solved.

Thus all the four roots of the equation (32) are found.

The constants A, B, C, D are to be determined from the following four initial conditions :—

At the instant $t=0$, the displacements of the hammer and the string are zero.

$$\therefore \quad y_0=0 \qquad \ldots \quad 37)$$

and $\zeta=0$. But $\zeta=y_0+u$,

$$\therefore \quad u=0 \qquad \ldots \quad (38)$$

Again, the initial velocity of the hammer is V, and that of the string is zero, since the hammer is elastic. Hence

$$V=\frac{d\zeta}{dt}=\frac{dy_0}{dt}+\frac{du}{dt}.$$

and

$$\frac{dy_0}{dt}=0 \qquad \ldots \quad (39)$$

$$\therefore \quad \frac{du}{dt}=V \qquad \ldots \quad (40)$$

The expressions for y_0 and u have been given in terms of $f(ct)$ in (27) and (29); hence, if we substitute these expressions in (37), (38), (39) and (40) and put $t=0$, we shall get four equations which are necessary and sufficient for determining the four arbitrary constants A, B, C, D.

If we divide the equation (32) by E and put $E=\propto$, which amounts to the assumption that the hammer is rigid, we shall get

$$\left(m+\frac{1}{3}\rho a\right)x^2+\rho\left(x+\frac{1}{a}\right)=0 \qquad \ldots \quad (41)$$

It will be seen that the solution of this equation is identical with that obtained by Kaufmann.

§ 3

Displacement during Impact.

In the author's previous paper it was shown that if $y_1\ y_0\ y_2$ were the displacements of the string for $x<0$, $x=0$ and $x>0$ respectively, and if ζ and u were respectively the displacement and compression of the hammer, then at any instant t defined by $n{\cdot}2a<ct<(n+1)2a$, these would be expressed in the following form :—

$$\left.\begin{aligned}
[y_1, y_2] &= \sum_1^{n+1} f_r(ct\pm x) - \sum_1^{n} f_r(ct+x-2a) \\
y_0 &= \sum_1^{n} f_r(ct - \sum_1^{n} f_r(ct-2a) \\
u &= \frac{2T}{E} \sum_1^{n+1} f_r(ct)
\end{aligned}\right\} \quad \ldots \quad (4)$$

$$\text{and } \zeta = y_0 + u \qquad \ldots \quad 42$$

If we write $\phi_r(z)=f'_r(z)$, then $\phi_r(z)$ is given by the result (2) of §1. Thus the differential co-efficients of y_0, y_1, y_2 with respect to t, *i. e.*, the velocities of different parts of the string are expressed as a finite series in $\phi_r(ct)$ and are therefore known.

Similarly $\frac{d\zeta}{dt}$ is expressed in terms of $\phi_r(z)$ and $\phi'_r(z)$.

The displacement ζ is expressed in terms of $\phi_r(z)$ and $f_r(z)$. Thus the velocities and displacements of both the hammer and the string are known, if we can find out $f_r(z)$, *i. e.*, if we can integrate $\phi_r(z)$. Now the integral of $\phi_r(z)$ takes a very elegant form in the case of the rigid hammer. So we confine ourselves to the treatment of this particular case only. The value of $\phi_{n+1}(z)$ for the case of the rigid hammer is very easily derived from the equation (51) of the previous paper by deleting the second part of the series, which involves β. Thus

$$\phi_{n+1}(z)=\frac{V}{c}e^{az_n}\Big\{1+{}^nC_1.az_n+{}^nC_2.\frac{a^2z_n^2}{\lfloor 2}+\dots\dots$$

$$+{}^nC_r.\frac{a^rz_n^r}{\lfloor r}+\dots\frac{a^nz_n^n}{\lfloor n}\Big\} \qquad \dots \quad (43)$$

where $z=ct$ and $z_n=ct-n\cdot 2a$.

By way of trial we write down the following series as a possible integral of $\phi_{n+1}(z)$:—

$$\frac{V}{ac}e^{az_n}\Big\{ah_n+{}^{n-1}C_1,\frac{a^2z_n^2}{\lfloor}+{}^{n-1}C_2.\frac{a^3z_n^3}{\lfloor 3}+\dots\dots$$

$$\dots\dots{}^{n-1}C_{r-1}.\frac{a^rz_n^r}{\lfloor r}+\dots\dots\frac{a^nz_n^n}{\lfloor n}\Big\} \qquad \dots \quad (44)$$

The differential co-efficient of this with reference to z_n is

$$=\frac{V}{c}e^{az_n}\Sigma({}^{n-1}C_{r-1}+{}^{n-1}C_r)\frac{a_rz_n^n}{\lfloor r}$$

$$=\frac{V}{c}e^{az_n}\Sigma{}^nC_r.\frac{a^rz_n^r}{\lfloor r}$$

$$=\phi_{n+1}(z).$$

Hence $f_{n+1}(z)$ is obtained simply by adding an arbitrary constant to the expression (44). Now $f_{n+1}(z)$ makes its appearance only at the instant $ct=n.\ 2a$, as is obvious from expression for y_0 in (41). But since the displacement of the string cannot change discontinuously the value of $f_{n+1}(z)$ at the instant $ct=n.2a$ is zero. But at $ct-n.2a$, we have

$z_n=0$. Hence the expression (44) vanishes, so that the constant of integration is zero. Thus we have

$$f_{n+1}(z)=\frac{V}{ac}e^{az_n}\left\{az_n+\sum_{2}^{n}{}^{n-1}C_{r-1}\cdot\frac{a^r z_n{}^r}{\underline{|r}}\right\} \qquad \ldots \quad (45)$$

In particular, we have

$$\left.\begin{aligned} f_1(ct)&=\frac{V}{ac}(e^{act}-1)\\ f_2(ct&=\frac{V}{ac}\cdot e^{a(ct-2a)}a(ct-2a)\end{aligned}\right\} \qquad \ldots \quad (46)$$

We are now in a position to examine the form of displacement of the string at different epochs. As the expression for y_0 is much simpler than that of y_1 or y_2 we first deal with y.

I Epoch $(o<ct<2a)$:—

$$y_0=f_1(ct)=\frac{V}{ac}(e^{act}-1). \qquad \ldots \quad (47)$$

II Epoch $(2a<ct<4a)$:—

$$y_0=f_1(ct)+f_2(ct)-f_1(ct-2a)$$

$$=\frac{V}{ac}\left[e^{act}+e^{a(ct-2a)}\{a(ct-2a)-1\}\right] \qquad \ldots \quad (48)$$

III Epoch $(4a<ct<6a)$:—

$$y_0=\sum_{1}^{3}f_r(ct)-\sum_{1}^{2}f_r(ct-2a)$$

$$=\frac{V}{ac}\left[e^{act}+e^{a(ct-2a)}\{a(ct-2c)-1\}\right.$$

$$\left.+e^{a(ct-4a)}\frac{a^2(ct-4a)^2}{\underline{|3}}\right] \qquad \ldots \quad (49)$$

$(n+1)^{th}$ Epoch $(n\,.\,2a < ct \leq n+1\,2a)$:—

$$y_0 = \sum_{1}^{n+1} f_r(ct) - \sum_{1}^{n} f_r(ct-2a)$$

$$= \frac{V}{aC}\Big[e^{act} + e^{a(ct-2a)}\,\{\alpha(ct-2a)-1\}$$

$$+ \sum_{r=2}^{r=n} c z_r \left\{\frac{z_r^{\,2}}{\underline{\lvert 2}} + \frac{{}^{r-2}C_1}{\underline{\lvert 3}}\, z_r^{\,3} + \frac{{}^{r-2}C_2}{\underline{\lvert 4}}\, z_r^{\,2} + \ldots\right.$$

$$\left. + \ldots \frac{{}^{r-2}C_1}{\underline{\lvert r-1}} \cdot z_r^{\,r-1} + \frac{z_r^{\,r}}{\underline{\lvert r}}\right\} \qquad \ldots \quad (50)$$

where $z_r = (ct - r\,.\,2a.)\alpha$

The expressions for y_1 are directly derived by writing $ct+x$ for ct in the above values of y_0. As for y_2, we know, it is given by

$$y_2 = \sum_{1}^{n+1} f_r(ct-x) - \sum_{1}^{n} f_r(ct+x-2a).$$

Since we consider here a rigid hammer only its displacement is the same as that of the string at the origin.

Thus the displacement of the rigid hammer and the string *during the impact* are all known.

§ 4

Displacement after Impact.

As long as the hammer presses against the string, the latter is bent at the point of contact. As soon as the hammer leaves the string, say when $t=t_1$, the string straightens out. So a new disturbance would arise at this instant, and spread from the origin in both dirctions. Let it be $\psi(ct \pm x)$. We assume that the original waves $\Sigma f_r(ct \pm x)$ continue to be generated at the origin. If any modification of this assumption is necessary, the very form of $\psi(ct \pm x)$ will automatically do that. Thus at any subsequent instant t, we have

$$\left.\begin{aligned} y_0 &= \psi(ct) + \sum_{1}^{n+1} f_r(ct) - \sum_{1}^{n} f_r(ct-2a) \\ y_2 &= \psi(ct-x) + \sum_{1}^{n+1} f_r(ct-x) - \sum_{1}^{n} f_r(ct+x-2a) \\ y_1 &= \psi(ct+x) + \sum_{1}^{n+1} f_r(ct+x) - \sum_{1}^{n} f_r(ct+x-2a) \end{aligned}\right\} \quad \ldots \quad (51)$$

The conditions that determine ψ are (1) that at $t=t_1$, the functions $\psi(ct_1)$—0, since there will otherwise be a discontinuous change in the displacement of the string at the origin, (2) that at $t=t_1$, the value of $\frac{dy}{dx}$ is continuous at the origin, *i.e.*,

$$\left(\frac{\partial y_2}{\partial x}\right)_{x=0} = \left(\frac{\partial y_1}{\partial x}\right)_{x=}. \qquad (52)$$

Substituting (51) in (52) we get after some reduction

$$\psi'(ct) = -\sum_{1}^{n+1} f'_r(ct),$$

$$\psi(ct) = -\sum_{1}^{n+1} f_r(ct) + \text{Contsant.}$$

But $\psi(ct_1) = 0$; hence the constant of integration is

$$\sum_{1}^{n+1} f_r(ct_1).$$

Therefore,

$$\begin{aligned}\psi(ct)&=\sum_{1}^{n+1}\{f_r(ct_1)-f_r(ct)\}\\ \psi(ct\pm x)&=\sum_{1}^{n+1}\{f_r(ct_1)-f_r(ct\pm x)\}\end{aligned}\tag{53}$$

Substituting (53) in (51) we get

$$[y_1,y_2]=\sum_{1}^{n+1} f_r(ct_1)-f_r(ct\pm x)$$

$$+\sum_{1}^{n+1} f_r(ct\pm x)-\sum_{1}^{n} f_r(ct+x-2a).$$

Now it should be borne in mind that since the wave $\psi(ct\pm x)$ originates only at the instant t_1, the distance traversed by it at any instant t on either side of the origin is $c(t-t_1)$. So the term $-f_r(ct\pm x)$ cancells the term $+f_r(ct\pm x)$, only as far as $x=\pm c(t-t_1)$. Thus, between $x=c(t-t_1)$ and $x=-c(t-t_1)$ we have

$$[y_1 y_2]=\sum_{1}^{n+1} f_r(ct_1)-\sum_{1}^{n} f_r(ct+x-2a)\tag{54}$$

and outside this region,

$$[y_1,y_2]=\sum_{1}^{n+1} f_r(ct\pm x)-\sum_{1}^{n} f_r(ct+x-2a)\tag{55}$$

We can interpret the above formulæ as follows :—

As soon as the impact terminates, each of these waves $f_r(ct\pm x)$ ceases to be generated, but as the rear-end of these waves or, more precisely, pulses, moves away from the origin, it is followed by a constant displacement $f_r(ct_1)$. It is thus obvious that $f_r(z)=f_r(ct_1)$ for all values of the argument z greater than ct_1. This amounts to saying that all these waves

$f_r(ct\pm x)$ continue to be generated at the origin, but subject to the condition that

$$f_r(ct\pm x)=f_r(ct_1) \qquad \dots \quad (56)$$

if $$ct\pm x \geqq ct_1$$

It has also been demonstrated in the previous paper that a wave $f_r(ct+x)$ makes its appearance at a point $(x, 0)$ only at the instant t given by $ct\pm x=r.2a$, and not before that. Thus to find how many direct waves are passing through a given point at a given instant t, we examine all the functions $f_r(ct\pm x)$ and retain only those, of which the argument is equal to or greater than $r.2a$. The same remark is true of their successive reflections also. For instance, consider the reflected pulse $f_3(ct+x-2a-4b)$. This begins to contribute to the displacement of the string, only if x and t are such that $ct+x-2a-4b<6a$.

Thus in order to draw the displacement-diagram of any point of the string we proceed as follows :—

First prepare a table of all the functional waves brought into existence during the impact and their successive reflections as shown below :—

$$f_1(ct-x), -f_1(ct+x-2a), +f_1(ct-x-2a-2b),$$

$$-f_1(ct+x-4a-2b), \text{ etc.}$$

$$f_1(ct+x), -f_1(ct-x-2b), \text{ etc.} \qquad \dots \quad (57)$$

$$\begin{cases} f_2(ct-x), -f_2(ct+x-2a), \text{ etc.} \\ f_2(ct+x), \text{ etc.} \end{cases}$$

Similarly proceed with f_3, f_4, etc., up to the last pulse generated by the impact.

Next, select some instant t, and examine the value of the argument of each of the above pulses. If the argument is greater than ct_1, write ct_1 for the argument, however large it may really be. Again, if it is a pulse of the f_1-type, reject it if the argument is less than zero; if the pulse is of the f_2-type, reject it if the argument is less than $2a$; if it is of the f_3-type, reject it if the argument is less than $4a$; and so on. Then the sum of all these functions so selected gives the total displacement of the string at the given point and given instant of time.

By the way, it should be pointed out that *the method is perfectly general* and is not confined to the case of the rigid hammer only.

We shall conclude this chapter with a numerical example. Let $\alpha = -\frac{2\rho}{m} = -0.02$, the striking length $a = 20$ *cm*, the distance b of the other end from the origin $= 80cm$, so that the total length of the string is 100 *cm* and its natural period is $200/c$ seconds. Then from the graph given in the next article, we find that the duration of impact $t_1 = 110/c$ approximately. For simplicity's sake we consider the displacement y_0 of the origin. We shall first show that the *displacement-time curve repeats itself from the instant* t_1 *with a periodicity* $200/c$.

Since $ct = 110cm$ and $2a = 40cm$, the impact has ended in the third epoch and only the pulses f_1, f_2, and f_3 have been brought into existence.

From formula (49) we see that, at the instant of termination of the impact, *i.e.*, at $t_1 = 110/c$, we have

$$y_0 = e^{110\alpha} + e^{70\alpha}(70\alpha - 1) + e^{30\alpha} \cdot \frac{(30\alpha)^2}{\underline{|2}} \qquad \ldots \quad (58)$$

We shall show that the value of y_0 at the instant $t = t_1 + 200/c$ will also be given by (58).

We see that the values of the arguments ct, $ct-2a$, $ct-2a-2b$, $ct-4a-2b$, $ct-2b$ are, 310, 270, 110, 70, 150 respectively; arguments of higher order are negative. Of these, the arguments ct, $ct-2a$, and $ct-2b$ are greater than ct_1 or 110, hence they may be each replaced by 110. The pulses of the f_3-type having argument $ct-2a-2b=70$, cannot contribute to the displacement. Hence, only the following pulses from the table (67) figure in the displacement:

$$f_1(310), -f_1(170), f_1(110), -f_1(70), -f_1(150),$$

$$f_1(110);\ f_2(310), -f_2(170),\ f_2(110), -f_2(70),$$

$$-f_2(150),\ f_2(110);\ f_3(310), -f_3(170),\ f_3(110),$$

$$-f_3(150),\ f_3(110).$$

Their sum is

$$y_0 = f_1(110) - f_1(70) + f_2(110) - f_2(70) + f_3(110)$$

$$= e^{110\alpha} + e^{70\alpha}(70\alpha - 1) + e^{30\alpha}\frac{(30\alpha)^2}{\lfloor\underline{2}} \qquad \ldots \quad (59)$$

We see that the expressions (58) and (59) of y_0 at t_1 and t_1+200/c respectively are identical. Hence the motion is periodic, and the period is the natural period of the string. Fig. 1 represents this displacement-diagram. It is to be noted that the part of the curve between $ct=150$ and $ct=160$ is straight and coincides with the t-axis.

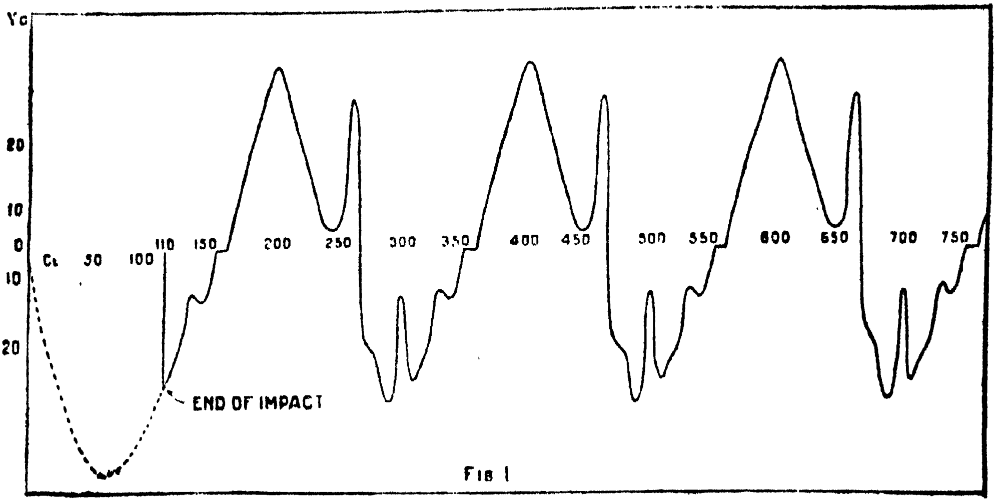

Fig I

STRUCK AND OBSERVED AT ONE FIFTH

§ 5

Duration of Impact.

The duration of impact is the root of the equation in t derived by equating the pressure of impact F_{n+1} to zero. Generally the equation cannot be solved algebraically even in the case of the rigid hammer. However if the striking-length a is small, so that the impact extends over several epochs, Newton's method of approximation to the roots of an equation helps us to some extent. For large values of a, we must depend on the laborious graphic method. If the impact terminates in the $(n+1)$ th epoch, the duration t_1 lies between $\frac{n.2a}{c}$ and $\frac{(n+1)2a}{c}$. Suppose that

$$ct_1 = \frac{1}{2}\left\{\frac{n.2a}{c}+\frac{(n+1)2a}{c}\right\}+x.a=(2n+1)a+xa.$$

Then the value of x is found by Newton's method to be

$$x=-\frac{1}{a}, \frac{F'_{n+1}\{(2n+1)a\}}{F_{n+1}\{(2n+1)a\}} \quad \ldots \quad (60)$$

Thus the duration of impact for a given value of a is given by

$$ct_1 = (2n+1)a - \frac{F_{n+1}'\{(2n+1)a\}}{F_{n+1}'\{(2n+1)a\}} \qquad (61)$$

If the value of x is positive and greater than a, then the impact extends into the next epoch. Hence the order number n of the final epoch is to be found from the condition that

$$|x| \leq 1. \quad \ldots \qquad (62)$$

When for a given value of n we find that $x=1$, the value of a that satisfies it is a limiting one, and if a is a little smaller than this limiting value, the impact extends into the next epoch.

We shall illustrate the method by a numerical example corresponding to the rigid hammer.

If a lies between $\propto$ and 32, the impact terminates in the second epoch and t_1 is given by

$$ct_1 = 2a - \frac{1}{a}\left(1 + e^{2aa}\right).$$

If a lies between 32 and 17 the impact terminates in the third epoch, and t_1 is given by

$$ct_1 = 4a + \frac{-(2+e^{2aa}) \pm \sqrt{2 + 2e^{2aa} - 4aae^{2aa} - e^{4aa}}}{}$$

When $a=17$, the impact extends into the fourth epoch, so ct_1 lies between $6a$ and $8a$.

Let $$ct_1 = 7a + x$$

Then by Newton's rule,

$$x = -\frac{F^4(7a)}{F'_4(7a)}$$

$$= -·08 \text{ approximately.}$$

Hence duration of impact is

$$t_1 = \frac{1}{c}(7a + x) = \frac{119{\cdot}17}{c}$$

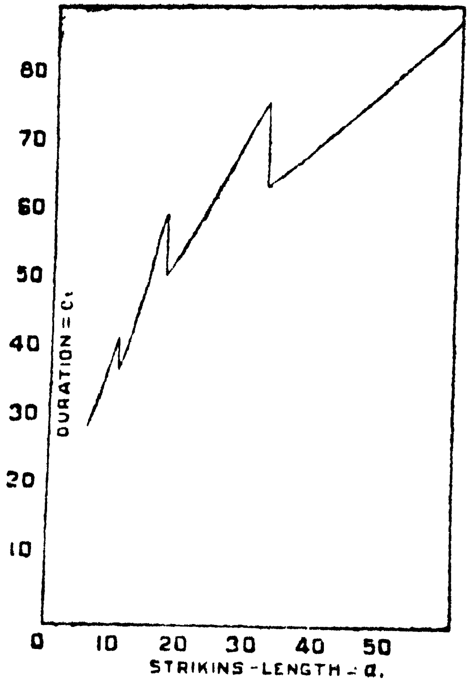

Fig 2

Fig. 2 represents a curve of duration of contact against the striking-length a. It will be noted that although the average slope of the curve is towards the origin, yet there are discontinuous changes in the value of t_1 from point to point, bringing into prominence a remarkable resemblance to the theoretical and experimental curves obtained by Raman and Banerji.[1]

A further numerical computation of the formulæ derived here will be made later.

I must conclude with my best thanks to Professor C. V. Raman for his very valuable advice and guidance in this work.

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[1] Proc. Roy. Soc. A., Vol. 97, 1920.

6. Annual Report for the year, 1925.

The Honorary Secretary begs to submit to the Committee of Management the following report on the activities of the Association during the year 1925.

PART I.

REPORT ON SCIENTIFIC INVESTIGATIONS.

1. The Scattering of Light by Liquid Surfaces.
2. The Molecular Scattering of Light.
3. Other Investigations.
4. List of papers published during the year.

PART II.

REPORT ON ADMINISTRATION.

5. Personal Matters.
6. Laboratory.
7. Library and Reading Room.
8. Workshop.
9. Financial Statement.
10. Acknowledgments.
11. Obituary.
12. Statement of Receipts and Expenditure and Balance-sheet for 1925.

PART I.

REPORT ON SCIENTIFIC INVESTIGATIONS.

It is proposed to give here a general account, in language as free from technicalities as possible, of the scientific results obtained by investigations carried out under the general direction of your Honorary Secretary in the Physical and Chemical Laboratories of the Association and published during the year 1925. It is hoped that such an account may be of interest to a wide circle of readers.

1. *The Scattering of Light by Liquid Surfaces.*

During the past few years the molecular scattering of light in fluids, *viz.*, gases, vapours and transparent liquids, has become a familiar subject in our laboratory. This phenomenon, which gives rise to the blue colour of the sky and of the sea, is a volume effect. Another equally important phenomenon was discovered in the course of work undertaken in our laboratory by Mr. L. A. Ramdas during the summer of 1923. This phenomenon is the scattering of light by the free surfaces of a great variety of liquids and has been extensively investigated by Mr. Ramdas.

When a beam of light is incident at the surface of separation of two media, a liquid and its vapour for example, part of the incident light is reflected and the rest refracted. A small fraction of the light is scattered by the molecules of the two media within both vapour and liquid. Besides these effects, careful observation shows that the part of the surface on which light is incident also scatters a small fraction of the incident light in all directions. Before going further into the matter, it is necessary to understand the nature of a liquid surface.

Nature of a Liquid Surface.

Whenever we wish to imagine an ideal plane surface we instinctively take the example of the surface of a liquid at rest. This is really a delusion, for, if we were to look at the surface of a liquid magnified say, a billion times, we would see it in a very turbulent state indeed, full of waves nearly as large as those which roll over a sea in a storm. We do not realise this because these waves are beyond the power of detection of our most powerful microscopes.

In a liquid the molecules have lost the great freedom of movement they had in the gaseous state, and, on account of the diminution of their extent of motion, the attraction of neighbouring molecules on each other becomes sensible. A liquid, in fact, is a moderately compact arrangement of molecules in which they still move about, but frequently colliding, over small ranges. At the surface, however, the conditions are special. Here the attraction which the molecules have for each other causes them to present a united front to disturbing forces. The surface is, in fact, comparable with a stretched elastic membrane. That is, it requires work to increase its area ever so little. But one should not think that the molecules at the surface are motionless. They also partake in the continuous movements and the more vigorous molecules occasionally fly off. Very often molecules of sufficient velocity collide against the surface and occasionally burst through the surface layer or knock out one of the surface molecules into the space above. We call this process evaporation. If the space above is enclosed, a stage is reached when the molecules escaping from the liquid equal in number those re-entering it. This continuous exchange of molecules between the liquid and vapour is accompanied by the continuous agitation of the surface. We may conceive the surface as full of waves and ripples owing to molecular bombardments, just like the surface of a pond disturbed by throwing stones. We are unable to see these waves and ripples because the lateral binding of the molecules at the surface into a thin elastic layer prevents the waves from becoming too large. To put it more accurately, we may say that the surface tension forms the controlling force which limits the degree of roughness of a liquid surface. This roughness is of molecular dimensions at ordinary temperatures.

As the temperature is raised, the molecules begin to move about with increasing vigour and the strength of binding of molecules at the surface diminishes and the kinetic energy or energy of motion of the molecules bombarding the surface also increases. This naturally results in the increased agitation or roughness of the liquid surface. As the temperature goes on increasing, for every liquid, there is a stage at which the surface tension tends to zero. At and above this temperature, known as the critical temperature, the molecules acquire so much energy that the liquid and vapour merge into a single gaseous phase. Above this temperature, no extent of compression can liquefy the gas. In the neighbourhood of the critical temperature we may expect the roughness of the liquid surface to increase to such an extent as to be visible even to the naked eye.

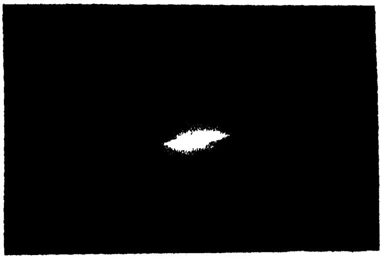
The above conception of a liquid surface is borne out by our experimental researches on the scattering of light by the surface over large ranges of temperature including the critical temperature.

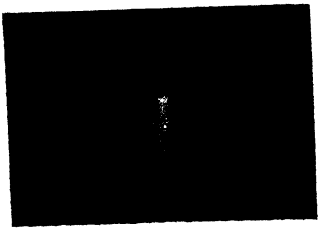
Opalescence of Liquid Surfaces.

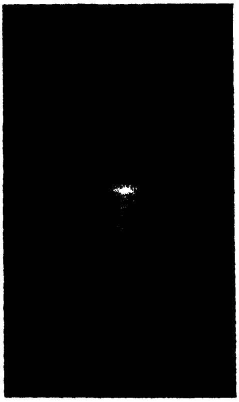
The method of observing the scattering of light by a surface is very simple. A strong beam of sunlight is focussed on the liquid surface and the surface observed in a direction adjacent to the refracted or reflected beam. At the place where the light falls on the surface may be seen a bluish-white or grey spot. Usually, however, the surfaces we handle are so dirty that the spot is very intense. The first thing necessary to observe the genuine scattering by the surface is to obtain the liquid perfectly free from dust and other contaminations both on the surface and inside the liquid.

This may be done by transferring the liquid into a distilling apparatus consisting of two fairly large glass bulbs connected by a communicating tube which has been thoroughly cleaned, washed and dried. The apparatus is [illegible] put under

Plate V







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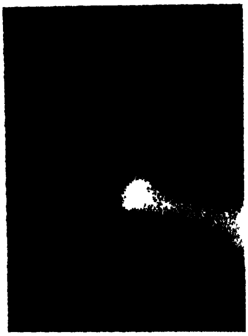

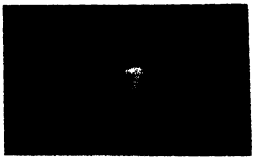

5.

6.

Surface-Scattering by Liquids

The Indian Photo Engraving Co., Calcutta.

the pump, exhausted and sealed off. The liquid is transferred to one of the two bulbs and slowly distilled over into the other bulb. When sufficient liquid has distilled over, it is shaken back into the first bulb. By repeating this process half-a-dozen times, all the dust and other impurities present in the liquid and the bulbs may be concentrated in the first bulb, and perfectly pure liquid having a clean surface finally distilled over into the second bulb. Nearly 65 transparent organic liquids and liquid mercury had been prepared in this way before the work on this subject was started.

The surfaces of these liquids, under the strong illumination referred to, were found to become visible by the light scattered by them, much in the same way as the surface of a piece of paper or plaster of Paris becomes visible to us by the light diffused by it in all directions. Unlike the surface of paper or plaster of Paris, however, the opalescent spots on the surfaces of the liquids were found to be perfectly structureless or continuous, thus showing that the roughness is of molecular dimensions and invisible. Actual observation in the case of these liquids brought out the relation that the intensity of scattering is inversely proportional to the surface tension, which is in agreement with the rule that a rougher surface scatters more light. Thus, water which has a surface tension of 72 dynes cm. scatters only $\frac{1}{4}$ of the light scattered by methyl alcohol whose surface tension is only 23 dynes cm. The intensity of scattering was measured for nearly 32 liquids and the results agreed with this relation.

Curiously enough the phenomenon of scattering was observed first in the case of liquid mercury which has a surface tension as large as 547 dynes and whose surface may be expected to scatter only $\frac{1}{10}$th of the light scattered by methyl alcohol. In fact the opalescent spot could only be observed when the background was very dark. This was secured by blackening the bulb outside and working in a dark room with a strong beam of sun-light focussed by a good condenser on the surface. The focal spot could then be observed as a faint bluish white spot. Our first communication on the subject[1] dealt with the very peculiar features of the light scattered by a mercury surface. In Fig. 6, Plate V, two elliptic patches are seen. This is a reproduction of the opalescent spot as viewed at about 30° with the liquid surface through a double image prism which is an optical contrivance for producing two images of our object, in which the vibrations constituting light are mutually perpendicular to each other. Thus the light-vibrations are vertical (*i.e.*, in the line joining the images) in the stronger image and horizontal in the weaker image. The contrast between the two shows that, parallel to the surface, the light of the opalescent spot consists only of vibrations that are perpendicular to the surface. The intensity of scattering in the same direction was found to be 10^{-8} times, or one ten-millionth part of the incident light per unit solid angle.

One very important difference comes in between the ordinary liquids,[2, 3] and liquid mercury. The scattering by the mercury surface is visible equally well in all directions even if the light is incident at an angle of 45°. In the case of the other liquids which, as remarked already, are rougher, the visibility is confined to the neighbourhood of the reflected and the refracted beams. This is what one should expect from the larger roughness of the surfaces. Figures 1 to 5 of Plate V illustrate the appearance of the surface opalescence of hexane for different directions of incidence and observation as mentioned in the description of the plates. The very interesting details of these phenomena have been described in full in the 2nd and 3rd papers.

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[1] C. V. Raman and L. A. Ramdas, Proc. Roy. Soc. A, Vol. 108, p. 561. (1925)—Part I.

[2] C. V. Raman and L. A. Ramdas, Proc. Roy. Soc. A, Vol. 109, p. 150 (1925)—Part II.

[3] C. V. Raman and L. A. Ramdas, Proc. Roy. Soc. A, Vol. 109, p. 272 (1925)—Part III.

Critical Temperature Phenomena.

As has been already mentioned, the surface tension of a liquid diminishes continuously and tends to zero as the critical temperature is approached. The effect of this will be to increase the roughness of the surface continuously until just below the critical temperature it becomes enormously large and the surface ceases to reflect any light. These effects have been studied in the case of liquid carbon-dioxide[1] which is a very convenient substance as its critical temperature is near the room temperature (31·35°).

A sealed bulb, a little over 1 cm. in diameter containing pure liquid carbon-dioxide prepared for a quantitative study of its internal light-scattering, was available and was used for the purpose.

Its temperature was regulated and maintained constant by immersion in a water-bath. On illuminating the liquid normally by a thin pencil, the surface opalescence could be observed at all temperatures and at 20° C was certainly several times brighter than in the case of hexane under equal illumination. It brightened up notably as the temperature approached 30°C. With further increase of the temperature up to the critical point, the surface-opalescence increases in a most remarkable way and becomes an exceedingly conspicuous phenomenon. Figs. 1, 2 and 3, Plate VI are photographs of the opalescent spot within the tube at temperatures of 30°, 30·35° and 30·6°C respectively The internal scattering in the liquid and in the vapour are also clearly seen in the photographs.

Interfacial Effects.

Very striking effects are also shown by the interface between two layers of a mixture of carbon-disulphide and methyl alcohol when its temperature is gradually raised up to the point at which the two liquids completely dissolve each other and merge into a single layer. The phenomena observed and the effect of raising the temperature to the critical solution point at which the two liquids are completely soluble in each other and the surface tension of the interface tends to zero, are very similar to those in the case of liquid CO_2, the layer below corresponding to the liquid and the one above to the dense vapour. Figs. 4 and 5 in Plate VI illustrate the enormous increase in the surface scattering which occurs as the temperature of the mixture is raised from 28° to 40°C.

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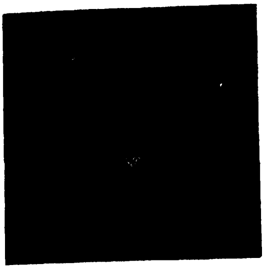
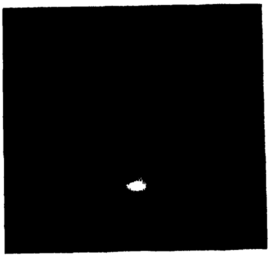
[1] See Paper III, Proc. Roy. Soc. A, Vol. 109, p. 272, 1925.

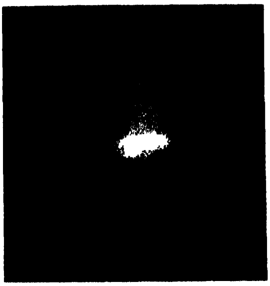
Oil Films on Water.

As is well known from the investigations of Rayleigh, Langmuir, Adam and others, the surface tension of water is greatly diminished when even a very minute quantity of oily matter contaminates its surface. For example, fragments of camphor which move about very vigorously on very clean water, are effectively stopped when the slightest trace of oil is spread on the surface of water. These writers have shown that the minimum quantity of any oil or organic compound like oleic or palmitic acid necessary to stop camphor movements completely, is equal to the amount necessary to cover the water surface with a mono-molecular film of the substance. It appeared therefore of great interest to determine how the surface opalescence of water is altered in such cases. It would be obviously too tedious and difficult to carry out the experiments on the effect of greasing and recleansing the water surfaces in vacuo. Fortunately, however, it is actually possible to make observations in the open. Distilled water is poured into a carefully cleansed glass dish painted dead-black outside, and the surface of the liquid is cleansed by blowing off the superficial layer. Sun-light is focussed upon the clean surface at about 45°, and the eye is placed so as to view the surface in a direction

Plate VI







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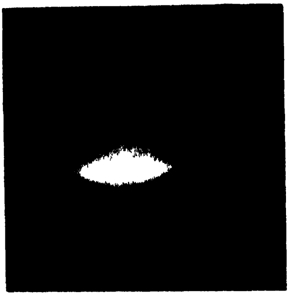

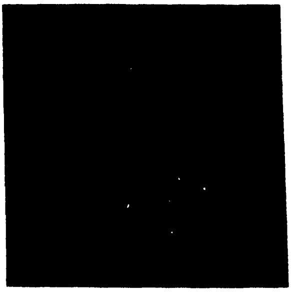

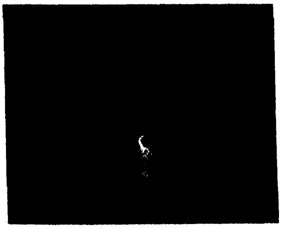

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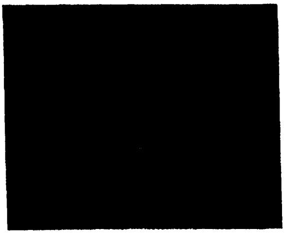
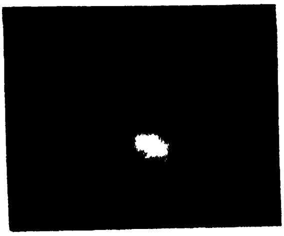


8.



Surface-Scattering by Liquids

The Indian Photo Engraving Co., Calcutta

nearly adjacent to the reflected rays. A screen with an aperture suitably placed is found very convenient, as it cuts off the regularly reflected light and all stray illumination, the illuminated water-surface being seen through the aperture. The internal scattering by the water is considerably increased by the presence of motes caught by the water from the air. Nevertheless, the superficial opalescence by clean water is readily observed with this arrangement as a greyish-white cap terminating the bluish-white internal track. Unless the air of the room is particularly free from dust, occasional dust-particles sail into view, are caught by the water surface and dragged down.

The effect of greasing the surface is readily observed; with a very minute quantity of oleic acid just sufficient to cover the whole surface with a film one molecule thick, judged by the stopping of camphor movements, the surface brightens up appreciably and is then more easily distinguished from the internal scattering. The increase in intensity is about 100 per cent. Figs. 7 and 8, Plate VI, show the phenomenon, the former being obtained with clean water and the latter when the surface is covered with a monomolecular layer of oleic acid.

Examined through a microscope, the greased surface shewed no trace of structure, the opalescence being perfectly uniform. When, however, the oleic acid used is in excess of the minimum required to stop camphor movements, a remarkable change takes place. The opalescence of the surface brightens up enormously, perhaps a thousand-fold. At this stage, shown in Fig. 9 in Plate VI the illuminated area on the surface is no longer continuous, as seen in a microscope, but is seen to contain an enormous number of micro-globules of oil. A micro-photograph of the surface at this stage is shown in Fig. 6 in Plate VI.

The presence of these mono-molecular films appears to alter the properties of the surface of water appreciably in other ways. Thus, according to certain writers, the process of evaporation at ordinary temperatures is said to be retarded to a great extent when the surface has a mono-molecular film of a substance like oleic acid. This is easily understood as the water molecules knocking against the surface from below have to overcome the resistance offered by the molecules of oleic acid which are marshalled in close array against them. Another interesting effect is the calming of the surface by "Pouring oil on troubled waters." No wonder then that the optical properties of the surface also change so remarkably and the intensity of scattering increases.

It is interesting to note that a freshly cleaved surface of mica which is a crystalline solid, does not scatter any light.[1] This is what may be expected from the perfectly regular arrangement of atoms in the crystal and the perfect planeness of the cleaved surface. In the case of a sputtered film of gold in contact with such a surface,[2] a very faint bluish-white opalescence, having only a fifth of the intensity of scattering by a mercury surface, may be observed.

Further work on surface-scattering is being pursued with success. The results will be mentioned in the next report.

2. *The Molecular Scattering of Light.*

Introduction.

As a result of the considerable amount of work done by our workers during the last three years, the subject of scattering has been developed on very solid foundations and its relation to the state of the scattering medium brought out in great detail. Thus the phenomenon has been observed and studied in the case of gases and vapours at various pressures and temperatures up to the critical state, and liquids starting from the critical temperature downwards, and shown to be intimately related to the state of aggregation of the medium. Besides this, the structure of molecules in its relation to the degree of polarisation of the scattered light has been worked out with great success and we have now reached a stage in the subject when we can actually find out the positions of and distances between the atoms which constitute the molecule, starting with a few simple polarisation measurements and a knowledge of the molecular refractivity.

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[1] L. A. Ramdas, Proc. Ind. Assn. for Cultn. of Sc., Vol. IX, Part II, p. 129 (1925).

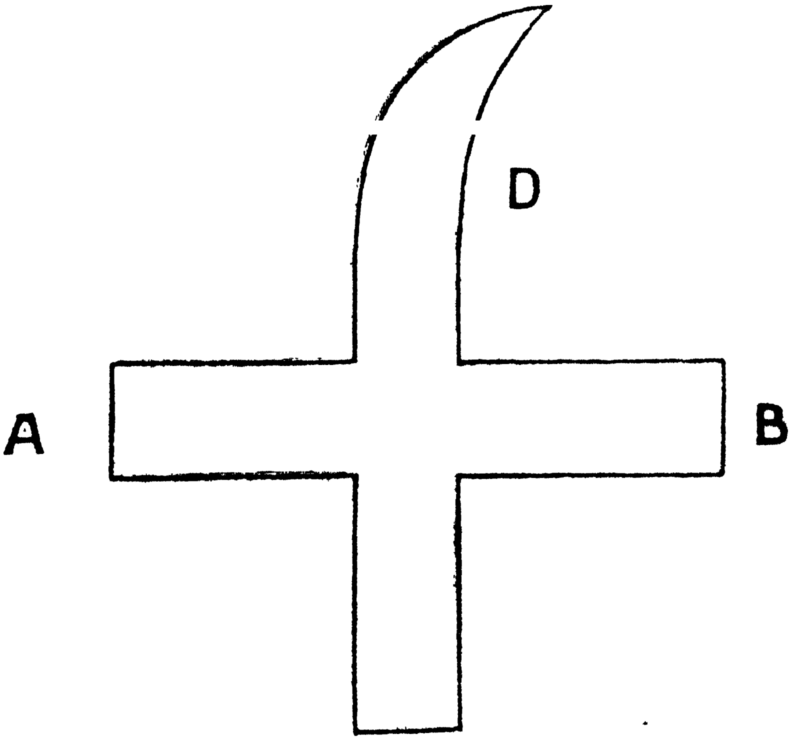
[2] L. A. Ramdas, Proc. Ind. Assn. for Cultn. of Sc, Vol. IX, Part IV, p. 323 (1926).

These results have been published in numerous papers which appeared in various scientific journals from time to time. In the following pages a general account of the subject is given, special emphasis being laid on the work done during the year under report.

Making Gases Visible.

When we look at the beautiful blue colour of the sky on a fine day, few perhaps except professional physicists would realise the exact nature of the part played by the molecules of oxygen and nitrogen in air in giving rise to this natural phenomenon. It was the late Lord Rayleigh who established from theoretical considerations, that the molecules which are present in the atmosphere are sufficient to give rise to the blue of the sky by reason of the light which they scatter.

This was actually verified in the most convincing manner by the experiments of Cabannes and the present Lord Rayleigh who observed the faint blue track of a strong beam of light passing through dust-free gases. This experiment is very easily tried in a place like India where we have brilliant sun-shine for the better part of the year. A metal cross-tube as in Fig. I closed at the three ends A, B and C by means of glass windows and provided with a smoothly bent horn of dark-green glass at the end D is the simple apparatus required. The horn is thoroughly blackened outside to prevent any light from getting in and a very strong, narrow beam of sun-light is passed horizontally through AB. When air or carbon-dioxide, rendered dust-free by passing through a tube filled with cotton-wool, is passed for a long time, the observer at C will find that the previously intense dusty track will get weaker and weaker until finally a perfectly uniform and faint blue track is left. This track is due to the light scattered by the molecules of the gas inside. The intensity varies in a very remarkable way when different gases are filled in the cross-tube. Thus, if the intensity of the track in pure hydrogen is taken as unity, air scatters four times, carbon-dioxide ten times, and carbon-disulphide vapour more than a hundred times as strongly.



Another very interesting feature of the light scattered in the transverse direction by these gases is that, when observed through a nicol, the track is almost completely extinguished when the shorter diagonal of the nicol (a nicol transmits only vibrations parallel to its shorter diagonal) is horizontal. There is some imperfection in the polarisation which can be measured as the ratio of the horizontal to the vertically polarised light in the track. The value of the imperfection of polarisation is very characteristic of each gas as it has a definite value in each case. Thus its value for hydrogen is 3·8%, for oxygen 9·4%, for nitrogen 4%, for carbon-monoxide 3·4%, for carbon-dioxide 10·6%, for carbon-tetra-chloride 1·9%, for argon ·5% and so on.

Thus we may conclude that so far as light-scattering by a medium is concerned, two quantities interest us, *viz.*, the intensity of the scattered light, and the imperfection of polarisation of the scattered light. We may now proceed to connect these quantities with the density, temperature, etc., of the gas or vapour.

In a gas the molecules have a free individual existence and, owing to their vigorous movements, between collisions, are in a state of chaos at any instant. The result of this is that, when a beam of light is passed through, the molecules which are in the path behave like individual sources of light, as it were, and scatter the light falling on them in all directions. Owing to the absence of any regularity in position of the different molecules, the light scattered by them has no definite phase relationship in any direction, except that of the incident beam, and each molecule contributes its mite to the total intensity. We may thus conclude that the intensity is directly proportional to the number of molecules per cubic centimetre or the density of the gas, the condition being that the contribution from each molecule arrives at random or in arbitary phases at the point of observation. The light thus scattered ought to be completely polarised, for we know that light-waves have transverse vibrations and we are observing at right angles to the incident beam.

A little consideration will show that the only vibrations which matter are those perpendicular to both the incident beam and the direction of observation. It has been mentioned, however, that the scattered light is not perfectly polarised. This is due to the fact that the individual molecules are not perfectly spherical. It is, therefore, clear that measurements of the percentage of imperfection of the scattered light in various gases and vapours at ordinary pressures (say one atmosphere) provide very valuable data for finding out the actual structure or shape of molecules.

During the last few years several interesting papers on the scattering by gases and vapours have been published by our workers here and during the present year Mr. A. S. Ganesan's measurements of the percentage of imperfection of polarisation of the scattering by nearly 32 organic vapours at one atmosphere pressure appeared in the Philosophical Magazine (June, 1925).

For his measurements Mr. Ganesan used a very big iron-cross blackened thoroughly inside and provided with suitable apertures to cut off all stray light and for limiting the length of the track for observation. For illumination a horizontal beam of sun-light was focussed by means of a big telescope objective and the light diverging from its focus refocussed at the centre of the cross by means of a suitable short-focus lens. As it is very essential to prevent distraction of the eye by external light and to keep the eye at its maximum sensitiveness to feeble illumination like that due to scattering, the observer located himself in a light-tight wooden cage 4 ft. square and 8 ft. high, facetiously known as "The Black Hole of Calcutta." In the wall in front of the observation end C of the cross-tube (see Fig. 1) and at the same height as the centre of the cross-tube was an aperture of about 4 cm. diameter through which the scattering track could be viewed. Under these conditions the scattering by any gas or vapour was a conspicuous phenomenon.

The imperfection of polarisation was measured in the following way.

A double-image prism (*i.e.*, an optical instrument which gives two images of an object the vibrations in one of which are parallel to the line joining the two images and the vibrations in the other are perpendicular to this direction) is adjusted in front of C so as to secure two images in the same line and adjacent to each other, one being the strong image with vertical vibrations and the other the feeble image with horizontal vibrations. In front of the double-image prism and in the observation aperture of the black hole is fixed a graduated circle with a good nicol mounted in it, so that, by simply turning the nicol and equalising the intensities of the two images in two alternate positions and noting the difference in the readings on the graduated circle, the imperfection may be calculated.

For accurate work it is essential that the vapour be pure and absolutely free from dust. In all cases Kahlbaum's chemicals were used. The liquid was evaporated from a glass retort and the vapour made dust-free by passing through a glass tube filled with cotton-wool. The cross-tube and the tube containing cotton-wool were kept at about the same temperature as the boiling point of the liquid used, by electrical heating. Before heating the retort, the dusty air in the cross-tube was driven out and replaced by dust-free air. On passing the vapour by boiling the liquid for a sufficiently long time, the cross-tube was filled with pure vapour. The polarisation measurements were then taken. Before beginning another vapour, the cross-tube was thoroughly heated and flushed with fresh air so as to get rid of the old vapour. The cotton-wool was also renewed every time.

As a result of his measurements for nearly thirty vapours, Mr. Ganesan comes to the conclusion that in the case of symmetrical molecules like CCl_4 the imperfection is as low as 1·9%, whereas for less symmetrical molecules like chloroform

(3·2%), carbon-di-sulphide (16·7%), and benzene (6·6%) the imperfection is much more. However, one cannot conclude that the longer a molecule is, the greater will be its anisotropy as shown by the imperfection of polarisation, for in the case of octane (2·7%) which is nearly twice as long as pentane (3·4%) the imperfection is less than in the latter case. We may assert this much that a geometrically spherical molecule has a minimum optical anisotropy, whereas geometrically unsymmetrical molecules have, in general, a larger optical anisotropy. We have to approach the problem in a slightly different way in order to correlate the measurements of imperfection of polarisation of the scattered light with the structure of the molecules. What we have to consider is the effect of the individual atoms constituting the molecule on each other in bringing about the observed optical anisotropy of the molecule as a whole. This very important problem was successfully worked out by Dr. K. R. Ramanathan in an interesting paper published in the Proceedings of the Royal Society[1] during this year. The main results are given below.

Influence of Molecular Structure.

It has been definitely established that light-waves are electro-magnetic waves in which what is propagated with the velocity of light is a periodic electric intensity and a periodic magnetic intensity which are at right angles to each other and to the direction of propagation. In most optical phenomena, what we are concerned with is the effect due to the electric field, that due to the magnetic field being negligible. When light-waves are incident on a molecule, we have to consider the action of the periodic electric field to which it is subjected. For our present purpose we may consider an atom as made up of a positive and an equal negative charge which ordinarily cancel each other. But when placed in a steady electric field, the two charges will undergo a relative displacement proportional to the intensity of the electric field, the force due to the attraction of these for each other tending to resist the displacement. In other words, the atom is polarised electrically and behaves like the electric analogue of a magnet. It acquires an electric moment in the field. When the incident field, as in our case, is periodic, the *atom* becomes a periodic doublet whose electric moment oscillates on either side of zero to a maximum value, just like the amplitude of a simple pendulum. In a *molecule*, therefore, we have as many such periodic doublets as there are *atoms* in the molecule. These influence each other in the incident electro-magnetic field, just as a system of magnets of known moments and known distances apart would influence each other. The electric moment of the molecule as a whole would therefore depend on the moments induced in each of the atoms and the effect of these on each other. The problem of the optical anisotropy of N_2O, CO_2, CS_2 and other molecules was worked out on these lines by Dr. Ramanathan. He has calculated, by assuming the electric polarisability of the individual atoms and their distances apart in these molecules, the percentage of imperfection of polarisation of the scattered light. The calculated values agree well with those actually observed. This very interesting study is being continued to the case of more complex molecules like benzene and cyclo-hexane.

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[1] Dr. K. R. Ramanathan, Proc. Roy. Soc. A, Vol. 107, p. 684, 1925.

Scattering by Dense Fluids.

We now come to another important aspect of the subject, *viz.*, its relation to the state of the medium. That the scattering by a gas would go on increasing proportionally to the density of the gas so long as it obeys Boyle's Law is not difficult to understand, for then the number of scattering molecules is proportional to the density of the gas. This is true only so long as the ratio of the actual space occupied by the molecules to the total space is negligible. When Boyle's Law fails at high pressures, the molecules can no longer be considered to be distributed at random and are, therefore, no longer independent scattering centres. In a paper published in the Philosophical Magazine (January, 1923, Raman and Ramanathan) it was shown that the intensity of scattering in these cases is proportional not to the number of molecules in unit volume, but to the square of that number, to the absolute temperature and to the compressibility of the medium. This is identical with the theory worked out for the case of the scattering by a medium near the critical temperature by Einstein and Smoluchowski on quite different lines.

The above results have been verified in detail in the case of ether,[1] vapour and liquid, and carbon-dioxide,[2] vapour and liquid, up to the critical temperature.

The intensity for the gas increases more rapidly than in proportion to the density of the medium, and on approaching the critical temperature becomes very large indeed as the compressibility becomes very large here. The polarisation becomes more and more perfect as the critical temperature is approached, but below it in the liquid state the compressibility becomes very small again and so the intensity diminishes rapidly, the polarisation also becoming less perfect.

We are thus naturally led to the case of liquids. That the scattering by liquids is also molecular in origin and that the theory of the phenomenon proposed by Einstein and Smoluchowski, which holds for the special case of the critical phenomena, hold not only for temperatures higher than the critical, *i.e.*, for dense gases. but also for the liquid state, was first pointed out in a paper[1] which appeared in the Proceedings of the Royal Society as early as 1922. In this paper the fact that the blue colour of the sea also arises from molecular scattering of sun-light falling on the sea was pointed out for the first time and was substantiated from theoretical as well as experimental grounds. Since then molecular scattering of light by a few transparent liquids had been studied and the results given in a paper published in 1923,[2] where it was shown that the results agreed with the theory of Einstein and Smoluchowski.

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[1] K. R. Ramanathan, Proc. Roy. Soc., A, Vol. 102, p. 151, 1922.

[2] C. V. Raman and K. R. Ramanathan, Proc. Roy. Soc., A, Vol. 104, p. 357, 1923.

During the year under review the very elaborate study of the phenomenon in the case of as many as 65 liquids made by Mr. K. S. Krishnan was published in the Philosophical Magazine.[3] The liquids were obtained from Kahlbaum and represented a fairly extensive series of organic compounds. They were the same as were used for the study of surface scattering and were contained in double-bulbs in which they had been obtained dust-free and pure by frequent distillation. The bulbs containing the pure distilled liquids were thoroughly blackened outside leaving only two windows in each for passing a parallel and narrow beam of sun-light and another for the observation of the blue tracks in a normal direction.

For the intensity and polarisation measurements the bulb was in each case immersed in water (when the refractive index of the liquid is small) or a suitable mixture of benzol and carbon-disulphide (when the refractive index of the liquid is large) contained in a rectangular glass tank. The glass tank was also blackened outside and corresponding windows left in it to allow the incident beam to get through the bulb and to observe in the transverse direction.

C. V. Raman, Proc. Roy. Soc., A, Vol. 101, p. 64, 1922.

C. V. Raman and K. Seshagiri Rao, Phil. Mag., Vol. XLV, p. 626, 1923.

K. S. Krishnan .Phil. Mag., Vol. 1, p. 697, 1925.

For the intensity measurements, the beam, before entering the bulb, passed through a block of homogeneous colourless Jena-glass, 2 cm. thick, and the blue tracks in the liquid and in the glass-block were compared by using a rotating sector photometer. By adjusting the open sectors, the intensities of the two tracks could be made to appear equal. The intensity measurements were thus obtained in terms of the scattering by the glass block and finally calculated in terms of the scattering by pure ethyl ether. These values were found to agree in most cases with the calculated values (except in the case of liquids having high refractive index like CS_2, and benzene-derivatives.

The percentage of imperfection of polarisation of the scattered light was measured in each case as described before, coloured screens being used when measurements were taken for different wave-lengths of light. For full details of the measurements and secondary effects due to feeble fluorescence in some of the liquids, reference may be made to the original paper.

The polarisation measurements show a general dependence on the structure of the molecules as in the case of vapours. Thus the almost completely symmetrical molecules of carbon-tetra-chloride and silicon tetra-chloride give rise to imperfections of polarisation of 6·1 % and 5·8 % respectively, whereas for benzene and toluene, etc., the values are 51 % and 59 % respectively. Another striking contrast is furnished by the unsaturated and saturated hydrocarbons and their derivatives, thus β-iso-amylene gives 25·8 % and isopentane gives 5·6 %, allyl bromide gives 59 % and propyl bromide gives 25 %, and so on.

Another noticeable feature with regard to the polarisation factors for the liquids calculated from the values for the vapours and those actually found is that the observed values are in most cases smaller than those calculated. This has been pointed out already by Dr. Ramanathan. Further work is required to correlate the actual nature of the liquid state with the nature of the same substance in its gaseous state.

In the foregoing account the influence of the anisotropy of the molecules on the intensity of the scattered light has been omitted. The effect is to inrease the intensity of the scattered light in the ratio $\frac{6(1+r)}{6-7r}$ where r is the percentage of the imperfection of polarisation. This correction factor has to be applied in the case of all media both liquid and gas or vapour.

3. *Other Investigations.*

(*a*) *Structure and Colours of Amethyst Quartz.*

The peculiar structure of amethyst quartz is well-known to be due to the repeated twinning of alternate layers of right-handed and left-handed quartz. When a section of the substance cut normal to the optic axes is viewed between crossed nicols, very beautiful patterns of alternately black and coloured fringes may be seen. This is usually explained as due to the superposition of the opposite rotations of the plane of polarisation produced by the two types of quartz, parts of the section-plate in which equal thickness of the two types occur appearing black, and other regions exhibiting colour varying with the thickness of the two kinds traversed by the light.

In a paper published in the Transactions of the Optical Society,[1] a new way of viewing these and other optical effects arising from the structure of amethyst has been suggested.

If we consider the planes separating the alternate layers of the two kinds of quartz to be perpendicular to the plate, a plane wave-front of circularly polarised light becomes corrugated as it has travelled with different velocities through the alternate layers. The corrugated wave-front should, according to well-known principles, give rise to diffraction effects and, at a distance from the crystal, resolve into sets of plane waves corresponding to diffraction spectra of the 1st, 2nd and higher orders on either side of the undeviated central pencil.

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[1] Prof. C. V. Raman, F. R. S. & K. Banerji. Trans. Opt. Soc., Vol. XXVI, No. 5 1924-25.

Effects supporting these considerations have been actually observed by passing unpolarised light from a pointolite lamp normally through the plate. Coloured diffraction fringes, arranged periodically and running parallel to the lines of the structure are seen in the field behind the plate. The section of amethyst may, in fact, be considered as a phase-change grating. The structure is not clear under the microscope with unpolarised light because the phase-changes are too gradual in that case. For fuller details and illustrations of the optical effects with polarised light, reference may be made to the original paper.

(*b*) *Is there really any " Total Reflexion ?"*

It is well-known that when a parallel beam of light is incident at the surface of separation of two media, if the incidence is from the denser to the rarer medium, there is a particular angle of incidence beyond which the regularly refracted beam vanishes and there is only total reflection of the incident light. According to the wave-theory, however, there exists in the second medium a disturbance which penetrates beyond the boundary to a depth depending on the angle of incidence. Some doubt has been thrown on the usual treatment of this phenomenon by Sir Arthur Schuster[1] who appears to hold that assumption made in the theory of an infinitely extended surface is essentially illegitimate. Sir Arthur Schuster has based his discussion of total reflection on an extension of the analogy between the case of refraction by a surface at *less* than the critical angle and the case of oblique transmission through a plane aperture bounded by straight edges. This error has been pointed out in a recent paper[1] by the writer where experiments are described and photographs are given, illustrating what *actually* happens in the case of total reflection by a surface of finite area, which is the case considered by Sir Arthur Schuster. A parallel pencil of light (green line of the mercury arc was used) whose aperture is limited by parallel straight edges, passes through a prism of glass, is incident on its second face and emerges nearly grazing the surface. Owing to the narrowness of the emergent pencil, it is spread out by diffraction, and the pattern seen through a telescope shows some remarkable features. It is strongly asymmetrical. When the incidence is increased beyond the critical angle, the principal band in the diffraction pattern disappears from the field, followed in succession by one or more of the others, but a great many remain and are just as distinctly visible as ever. The intensity of these bands diminishes relatively slowly. The results fit in very well with Dr. Chukerbutti's earlier work on the case in which the incidence is at less than the critical angle and do not support Schuster's considerations.

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[1] Proc. Roy. Soc., A, 107, p. 15.

(*c*) *On Brewster's Bands.*

In a paper on this subject by the writer and S. K. Datta,[2] the explanation of Brewster's bands and other allied phenomena from the new and very suggestive standpoint proposed by Schuster[3] has been considered. When monochromatic light is reflected by or transmitted through two parallel plates in succession, we have a superposition of the Haidinger ring-systems due to the two plates in the sense that the observed intensity in any direction is the product of the intensities due to either plate separately. Illustrations showing the effect of such superposition in various cases have been reproduced in the paper, differential and summational fringe systems of various orders being observable. When non-homogeneous light is used, the Haidinger fringes disappear and along with them also the superposition pattern, leaving only a uniform illumination in the field, except in the special case of the differential system of the first order for two plates of equal thickness. A simple geometrical explanation is thus forthcoming why Brewster's bands can be observed even in non-homogeneous light with thick plates in this case.

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[1] Prof. C. V. Raman, F.R.S., Phi. Mag., Vol. 50, p. 812, 1925.

[2] Prof. C. V. Raman and S. K. Dutta, Trans. Opt. Soc., Vol. XXVII, No. 1, 1925-26.

[3] Schuster, Phil. Mag., 48 Oct. (1924), 609-619.

4. *Papers published during the year.*

Proceedings of the Indian Association for the Cultivation of Science, Vol. IX, Part II.

1. The Polarisation of Resonance Radiation and the Duration of the Excited State—by K. R. Ramanathan, M.A., D.Sc.
2. Prevision of Earthquakes—by Hemchandra Das-Gupta.
3. On the Motion generated in a Viscous Liquid by the Translation of Certain Quartic Cylinders—by Subodh Chandra Mitra, M.A.
4. The Scattering of Light by Solid Surfaces—by L. A. Ramdas, M.A.
5. Forced Vibrations of Finite Amplitude of Stretched Strings—by R. N. Ghosh, M.Sc.
6. Surface Tension of Water, Benzene, Methyl and Ethyl Alcohols—by Barkat Ali, M.Sc.

Vol. IX, Part III.

1. On the Fusion of Crystalline Solids—by K. R. Ramanathan, M.A., D.Sc.
2. The Water-Spark Absorption Spectra of Copper—by P. K. Kichlu, M.Sc.
3. Experimental Study of the Elastic Impact of Pianoforte Hammer—by R. N. Ghosh, M.Sc., and J. N. Dey, M.Sc.

Proceedings of the Royal Society.

1. The Structure of Molecules in relation to their Optical Anisotropy—Part I, by K. R. Ramanathan, M.A., D.Sc.
2. The Scattering of Light by Liquid Boundaries and its Relation to Surface Tension—Part I—by C. V. Raman, F.R.S., and L. A. Ramdas, M.A.
3. The Scattering of Light by Liquid Boundaries and its Relation to Surface-Tension—Part II, by C. V. Raman, F.R.S., and L. A. Ramdas, M.A.
4. The Scattering of Light by Liquid Boundaries and its Relation to Surface-Tension—Part III, by C. V. Raman, F.R.S., and L. A. Ramdas, M.A.

Philosophical Magazine.

1. On the Molecular Scattering of Light in Liquids—by K. S. Krishnan.
2. The Nature of the Disturbance in the Second Medium in Total Reflexion—by C. V. Raman, M.A., D.Sc., F.R.S.

3. On the Polarisation of Light Scattered by Organic Vapours—by A. S. Ganesan, M.A.

Physical Review.

1. On the Scattering of Light in Mixtures of Air and Carbon-dioxide—by Durgadas Banerjee, M. Sc.
2. Transparency and Colour of the Sea—by K. R. Ramanathan, D.Sc.

Nature.

1. Anomalous-Dispersion and Multiple Lines in Spectra —by Prof. C. V. Raman, F.R.S., and S. K. Datta, M.Sc.
2. The Spectrum of Potassium excited during its Spontaneous Combustion with Chlorine—by L. A. Ramdas, M.A.
3. The Structure of Benzene and Cyclo-Hexane and their Optical Anisotropy—by Dr. K. R. Ramanathan.

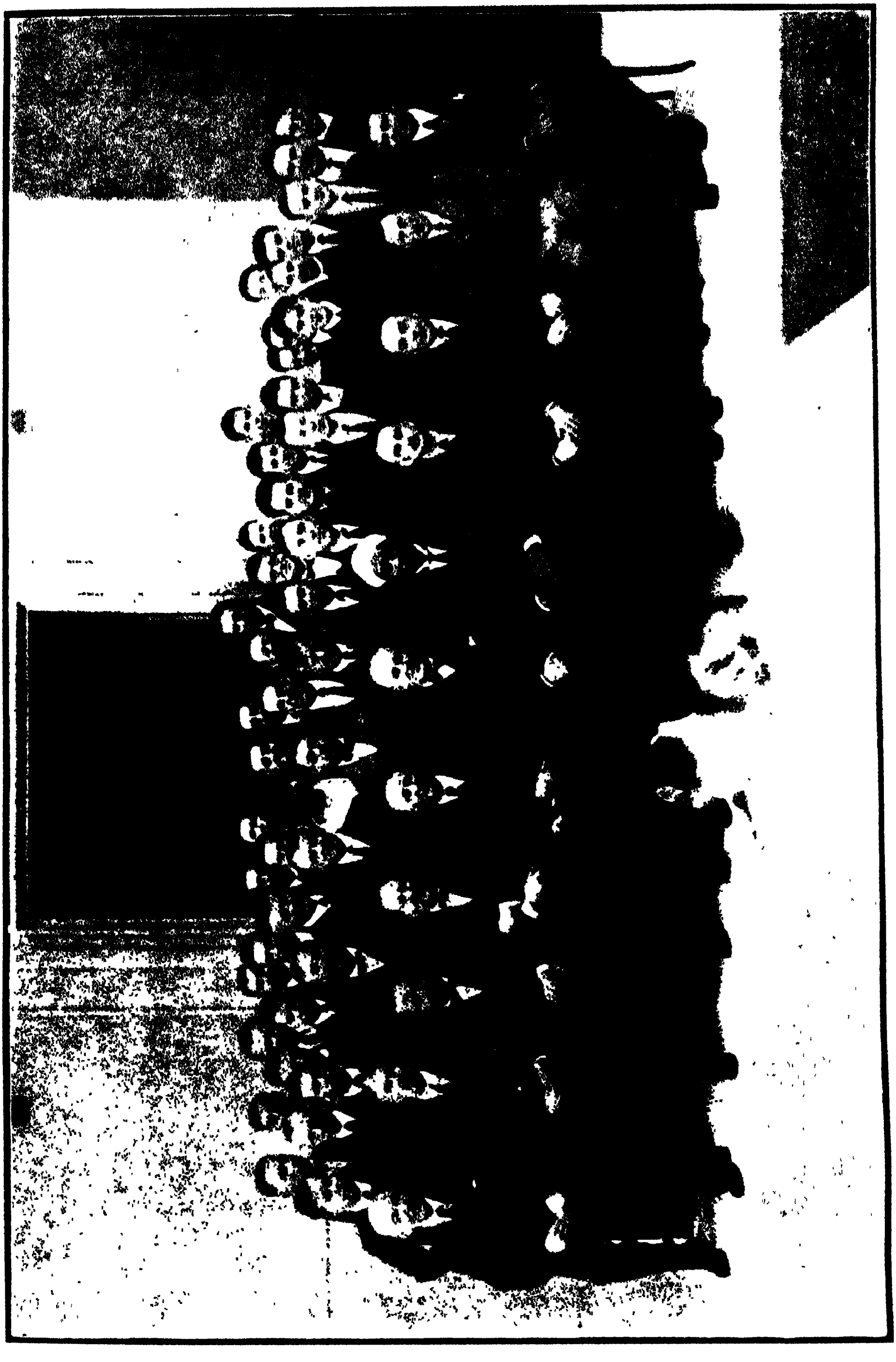
Quarterly Journal of the Indian Chemical Society.

1. A Critical Study of the Methods of Analysis of Lignin—by S. Venkateswaran.

Transactions of the Optical Society of London.

1. The Optical Properties of Amethyst Quartz—by Prof. C. V. Raman, F.R.S., and K. Banerjee, M.Sc.

Plate VII



Group at Norman Bridge Laboratory of Physics, Pasadena, California

2. On Brewster's Bands—Part I—by Prof. C. V. Raman, F.R.S., and S. K. Datta, M.Sc.

PART II.

ADMINISTRATIVE REPORT.

5. *Personal Matters.*

Mention was made in the report for the previous year regarding your Honorary Secretary's stay at the California Institute of Technology, Pasadena, as a Research Associate. After completing an extensive course of lectures on light-scattering, your Honorary Secretary, at the invitation of Prof. D. L. Webster, visited the Stanford University at Palo Alto, California, and lectured early in January and later left for Toronto where he lectured at the Royal Canadian Institute. Next followed visits to the New York Western Electric Company's laboratories and to the General Electric Company At Schenectady. At the latter place he had the opportunity of meeting the well-known physicists Langmuir, Hull, Coolidge and others who are on the staff of the General Electric Company.

Returning *viá* England towards the end of January, your Honorary Secretary took the opportunity of visiting the scientific Institutes in Norway, Sweden and Denmark. In Norway he visited Bergen at the invitation of the distinguished meteorologist Prof. Bjerknes who presides over the Geo-Physical Institute. Visits were also made at Oslo to the Mineralogical and X-ray laboratory of Prof. Goldschmidt and to the laboratory of Prof. C. Störmer who is devoted to the study of one of the most beautiful and marvellous of natural phenomena, *viz.*, the Aurora Borealis. From Oslo, he next proceeded to Stockholm where he visited the world-famous Nobel Institute under Prof. Svante Arrhenius, the University Laboratories and the Metallurgical Institute of the University. A short visit was also made to the University of Upsala where a very pleasant day was spent visiting the Physico-Chemical laboratory of Prof. Svedberg. Your Honorary Secretary then visited Copenhagen where he had the valued opportunity of meeting Prof. Niels Bohr, one of the most outstanding personalities in the scientific world of to-day. He had a very interesting discussion with the great scientist on modern problems in Physics. Leaving Copenhagen, the laboratories of Prof. Nernst at Berlin and the College de France at Paris were also visited. After this very extensive and interesting tour through America and Europe, your Honorary Secretary returned to India in the middle of March. After a spell of some five months' hard work in Calcutta, your Honorary Secretary, at the invitation of the Russian Academy of Science to attend its bicentenary celebrations, again left India in the middle of August and reached Russia in time to attend the celebrations of the Academy at Leningrad and Moscow. The greetings of the Association were presented to the members of the Academy on the occasion and, as a representative from India, he was received with great enthusiasm throughout Russia. He was invited to lecture on the Structure of Benzene before the Mendeleff Congress of Chemistry at Moscow, and also paid a visit to the University of Tiflis in Georgia. The return journey to India was made *viâ* Leningrad, Berlin, Paris, Switzerland and Italy, Calcutta being reached again in the third week of November.

As usual the Association attracted workers from various parts of India who carried out researches on various problems.

Dr. K. R. Ramanathan of Rangoon spent his summer vacation here and was engaged in his theoretical investigations on the structure of Benzene and Cyclo-hexane.

Mr. C. M. Sogani of the Benares Hindu University carried out a very interesting piece of research on the scattering of light by chromatic emulsions, during the summer.

Mr. V. M. Dhabadghao of Amraoti College, Central Provinces, worked here during the summer vacation with the concave grating and made some preliminary studies with the absorption spectra of sulphur vapour.

Mr. Durgadas Banerjee, Lecturer, University College of Science, worked in our Laboratory on the scattering of light by gaseous mixtures at ordinary pressures.

Mr. L. A. Ramdas, Palit Research Scholar, was engaged during the year in his investigations on the scattering of light by liquid surfaces and on the origin of camphor movements on water and allied phenomena.

Mr. K. S. Krishnan, Research Scholar of the Association carried out a series of investigations on the scattering of light by nearly 65 organic liquids, on the diffraction of light by spherical obstacles and on a new phenomenon observed by Glaser in diamagnetic gases.

Mr. Sushilkrishna Datta of St. Xavier's College, was working on Brewster's Bands.

Mr. I. Ramakrishna Rao, Research Scholar of the Association, was engaged in the study of diffraction of light by straight and round edges, diffraction by emulsions and the scattering of light by organic vapours.

Mr. Kedareswar Banerji, Palit Research Scholar, was engaged in his investigations on the permanent deformations due to contact of solids.

Mr. S. Venkateswaran of the Government Test House, Alipore, was working in the Chemical Laboratory on the methods of analysis of lignin. He was also engaged in the study of light-scattering by electrolytes and by chromatic emulsions.

Towards the end of the year Mr. V. I. Vaidyanathan from Travancore joined the Association and took up an important piece of research in Magnetism. He began his work on the diamagnetic susceptibility of gases at low pressures.

Mr. K. Krishnamurti from Vizianagram was working during the latter part of the year on the scattering of light by amorphous solids and under-cooled liquids.

Mr. C. Mahadevan who joined us towards the end of the year was investigating the structure of fiery opal.

Mr. Bhupendranath Banerjee was engaged in the study of total-reflection phenomena.

Mr. Girindranath Chuckerbutty did preliminary work with the Quartz Spectrograph.

6. *Laboratory.*

Since the return of your Honorary Secretary from his American tour the Physical and Chemical Laboratories have been thoroughly overhauled and the special grant of Rs. 10,000 given by the Government of India during the year enabled a start to be made towards renovating and modernising our equipment. The electrical installation which had served for several years was completely renewed, arrangements being made to give independent switch boards and connections for each room. The water and gas fittings, which were previously taken through the flooring were laid across the ceiling and a sufficient number of gas and water taps were provided for each room. The almirahs containing valuable apparatus were all rearranged so that different rooms could be allotted for work on X-rays, on Light-Scattering, on Spectroscopy, on Magnetism and on Sound.

As a result of the present rearrangements, the Association can now provide space for a great number of research-students to work conveniently on the various branches of Physics and Chemistry.

The following additions have been made during the year to our stock of apparatus :—

1. One Maudsly's Rotary Converter with starter, the A. C. output being 20 amperes at 160 volts.
2. One D. C. Ammeter.
3. One A. C. Voltmeter.
4. One A. C. Ammeter.
5. One 1000 C. P. Ediswan Pointolite.
6. One Resistance and holder for 100 C. P. Pointolite.
7. One Beckmann Thermometer.
8. One F/3 slit for grating.
9. Two Silica Burners.
10. One Chronometer (2 day).
11. One 6-volt accumulator.
12. Special glass bulbs for the study of scattering by vapours
13. 36 double-bulbs for liquid scattering.
14. 12 Pyrex glass bulbs for scattering work.
15. Two hundred feet of cinematographic film for recording the movements of amyl alcohol droplets on water.
16. A motor for the Rotating sector Photometer.
17. One oblong glass cell for Projection.
18. 6 circular glass basins for projection.
19. Wire and insulators for Antenna.
20. One box for lantern-slides.
21. Glass stop-cocks.
22. Microscope slides and cover-glasses.
23. A few samples of Opal.
24. A few different makes of electric bulbs, for the distillation of sodium.
25. One Underwood Type-writer.

7. *Library and Reading Room.*

The big well-lighted hall previously used as a lecture-hall for the Botany students has now been converted into an excellent reading-room and library. The very valuable

journals and books belonging to the library have been arranged neatly in the hall and long tables, provided with racks for keeping current numbers of the foreign publications, placed along the centre of the hall, for the use of readers.

The following special additions to the library were made during the year :—

1. The Moon Element by E. E. Fournier de Albe.
2. The Electron by R. A. Millikan.
3. Wireless Telephony and Broadcasting by H. M. Dowsett in two Vols.
4. Electronen Rohren by Dr. Barkhausen.
5. Electrical Engineering by W. T. Macall.
6. Alternating Currents by Alfred Hay.
7. Alternating Current Electrical Engineering by W. T. Macall.
8. Magnetos by A. P. Young.
9. Photo-Electricity by Stanley Allen.
10. Higher Mechanics by Horace Lamb.
11. Hand-buch der Spectroscopie by H. Kayser and Konen, Vol. VII.
12. The Theory of Relativity by L. Silberstein.
13. Dictionary of Applied Physics in 5 Volumes by Sir R. T. Glazebrook.

The following publications were subscribed for as usual :—

1. The Scientific American Monthly.
2. Nature.
3. Science Abstracts, A. and B.
4. American Journal of Science.
5. Philosophical Magazine.
6. Botanical Gazette.
7. Annals of Botany.
8. Astrophysical Journal.
9. Chemical News.
10. Proceedings of the Royal Society, A. and B.

11. Transactions of the Royal Society, A. and B.
12. Physical Review.
13. Annalen der Physik.
14. Physikalische Berichte.
15. Zeitschrift fur Physik.
16. Physikalische Zeitschrift.
17. Encyklopadie der Mathematischen Wissenschaften.
18. Collegian.

We have to acknowledge with thanks the presentation of journals and periodicals in exchange for our Proceedings from the following societies and institutions:—

1. The Smithsonian Institution.
2. Cambridge Philosophical Society.
3. Physico-Mathematical Society, Tokyo, Japan.
4. Manchester Literary and Philosophical Society.
5. American Philosophical Society.
6. University of Illinois.
7. Akademie der Wissenschaften—Leipzig.
8. Franklin Institution.
9. American Geographical Society.
10. South African Association for the Advancement of Science.
11. The Prussian Academy of Sciences, Berlin.
12. The Academy of Sciences, Vienna, Austria.
13. University of Pennsylvania, Philadelphia.
14. University of Philadelphia.
15. The Physical Society of France.
16. Royal Canadian Institute.
17. Bureau of Standards.
18. University of Iowa.
19. University of Calcutta.
20. Calcutta Mathematical Society.
21. Reale Academia Nazionale Dei Lincei, Rome.
22. Societe De Phyzique Et D' Histoire'—Naturelle-Geneve.
23. Journal of the Chemical Society, London, and British Chemical Abstracts, from Rai Chuni Lal Bose Bahadur, C.I.E.

23. Bayerischen Akademie der Wissenschaften—Munchen.
24. Der Gesselschaft der Wissenschaften, Göttingen.
25. Government of India.
26. Government of Bengal.
27. Government of Mysore.
28. University of Bombay.
29. University of Allahabad.
30. Agricultural Research Institute, Pusa.
31. Asiatic Society of Bengal.
32. Indian Institute of Science of Bangalore.
33. The Geological Survey of India.
34. The Indian Chemical Society.

The following additional journals have been subscribed for during the year.

1. Journal of the American Chemical Society.
2. Journal of Physical Chemistry.
3. Proceedings of the National Academy of Sciences, Washington.
4. Zeitschrift fur Kristallographie.
5. Zeitschrift fur Physikalische-chemie.
6. Annales de Physique.

The thanks of the Association are due to the Editors of the Englishman, Forward, Bengalee, Servant and Basumati for gratuitously supplying copies of their daily to the library and for publishing in their columns our daily Meteorological Reports.

8. *Workshop.*

The Workshop of the Association continued to function as a valuable auxiliary to our Research Laboratories and the mechanics turned out the following appliances :—

1. One two-mirrors Heliostat (Complete).
2. One Shearer X-ray tube with different anticathodes.
3. One Rotating Sector Photometer.
4. One Sieghban's X-ray Tube.

5. Twelve brass clamps.
6. Three graduated circles for mounting nicols.
7. Mounting with worm-screw and wheel for interference plates.
8. Repairing of the centrifugal pump.
9. Two big stands.
10. Fitting rollers for the grating camera.
11. Fitting diaphragms for the camera.
12. One stand and frame for a big mirror.
13. Six small stands.
14. One hot-air-oven of copper.
15. One resistance fitted in iron frame with regulator and switch.
16. One circular gas burner.
17. A few screw-taps.
18. A toothed wheel for hand-drill.
19. One coupling for milling machine chuck.
20. A shaking apparatus.
21. A heavy all-brass stand for big electro-magnet.

Besides these, several minor repairs of instruments were carried out.

The following tools were purchased for the work-shop :—

1. One six-inch four jaw three steps chuck.
2. One complete set of drills.
3. A few dozen hack saw blades, etc.

9. *Financial Statement.*

During the year under report, the Government of India gave us a special grant of Rs. 10,000 in aid of our scientific work and our grateful acknowledgments are due to them for this timely support.

On the 31st December, 1925, the Association had in the custody of the Imperial Bank of India, Government Securities to the value of Rs. 2,35,400 in the general fund, Rs. 6,000 in the Ripon Professorship fund, Rs. 500, for the Nikunja

Garabini Medal fund, a floating balance in the bank of Rs. 8,592-2-5 and a cash balance in the office of Rs. 150-12-0 amounting in all to Rs. 2,50,612-14-5.

On the 31st December, 1924, the Association had in the custody of the Imperial Bank of India, Government Securities to the value of Rs. 2,32,400 in the general fund, Rs. 6,000 in the Ripon Professorship fund, Rs. 500 in the Nikunja Garabini Medal fund, a floating balance in the bank of Rs. 3,657-5-6 and a cash balance in the office of Rs. 3,698-6, amounting in all to Rs. 2,46,255-11-6.

A copy of our balance-sheet and of the Receipts and Expenditure during the year is attached to the report.

The thanks of the Association are due to Babu Nirmal Chunder Chunder, M.A., B.L., who has been kind enough to continue his annual subscriptions.

10. *Acknowledgments.*

The thanks of the Association are due to the Honorary Engineers, Rai Krishna Chandra Banerjee Bahadur, Babu Bhavadev Chatterji, Babu Buth Nath Chakravati, to the Honorary Legal Advisers, Babu Jatindra Nath Basu and Babu Nirmal Chunder Chunder, to the Honorary Auditor, Babu Ishan Chandra Bose, to the Honorary Secretary, Prof. C. V. Raman and to the Honorary Assistant Secretaries, Babu Jyotish Chandra Pal and Babu Ashutosh Dey for their gratuitous services.

11. *Obituary.*

During the year under report the Association sustained a heavy loss by the death of Atul Chandra Datta who was an earnest member and used to take a keen interest in its cause. The Association recorded its deep sense of sorrow at his death and a copy of the letter was forwarded under the signature of Rai Bahadur Dr. Chunilal Bose, Vice-President, to his son Babu Ramesh Chandra Datta on the 11th March, 1925.

Dr.

Receipts and Expenditure during

	Rs.	A.	P.
Subscription account	307	0	0
Rent from Shops	4,332	0	0
Miscellaneous account	938	4	0
Interest account, General Fund	8,020	1	0
Ripon Prof. Fund	190	0	0
Nikunja Garabini Fund	17	8	0
Jatindra Ch. Prize Fund	19	4	0
Woodburn Medal Fund	17	8	0
Dr. Sircar Medal Fund	105	0	0
Fees from Students	7,382	10	0
Bulletin, etc., Sold account	155	9	0
Provident Fund account	566	11	9
Old Material Sold account	47	11	9
Dr. Sircar Memorial Fund	717	0	0
Deposit from students	40	0	0
Discount account	984	12	8
Donation account	50	0	0
Post Office Savings Bank account	20	0	0
Suspense account	374	10	0
Government of India Grant account	10,000	0	0
Floating Balance in the Imperial Bank on 31st December, 1924	3,657	5	6
Cash in Office on 31st December, 1924	3,698	6	0
	41,641	5	11

Certified that the accounts for the year 1925 have been audited and found correct.

I. C. Bose,

Honorary Auditor.

Cr.

the year ending 31st December, 1925.

	Rs.	A.	P.
Government Securities 3½% General Fund	3,000	0	0
Commission account, General Fund	25	14	0
Ripon Prof. Fund	1	6	0
Nikunja Garabini Fund	0	3	0
Contribution to Provident Fund	158	10	9
Building Repairs account	1,116	11	0
Building Reconstruction account	377	1	0
Scientific Instruments account	1,759	0	6
Municipal Tax account	2,324	6	0
Charges of Gas (Oriental Gas)	316	5	9
Charges of Electric (Electric Supply Corp.) ...	844	2	6
Provident Fund account	2,891	8	9
Postage Stamp account	236	3	6
Printing Charges account	338	11	6
Laboratory Charges account	1,684	5	6
Library account	1,355	1	0
Establishment account	6,528	0	6
Electric Installation account	2,031	6	6
Furniture account	425	1	6
Botany class account	2,176	4	0
Charges General account	1,244	15	8
Gas and Water Fittings account	592	0	6
Miscellaneous account	657	3	0
Post Office Savings Bank account	1,094	10	0
Trivandrum Fund account	400	0	0
Suspense account	482	0	9
Tools and Implements account	36	8	0
Workshop Instruments account	22	12	0
Vizianagram Fund account	450	0	0
Workshop Petty Charges account	338	3	9
Floating Balance in the Bank on 31st December, 1925 ...	8,592	2	5
Cash in Office, on 31st December, 1925	150	12	0
	41,641	5	11

C. V. RAMAN,
Honorary Secretary.

Dr.

Balance sheet as on

	Rs.	A.	P.
Government Securities, 3½% General Fund	2,35,400	0	0
Do. Ripon Prof. Fund	6,000	0	0
Do. Niknnja Garabini Fund	500	0	0
Range of Shop (East Side)	2,516	10	9
Do. (West Side)	2,308	5	0
Visianagram Laboratory	40,900	14	0
Value of land and Old building	31,680	11	9
Lecture Hall and Gallery	23,465	5	3
Observatory	3,329	9	9
Servants' Quarters	1,024	0	0
Darwan's room	803	13	9
Bonus of Provident Fund	1,922	0	0
Contribution to Provident Fund	2,360	12	1
Scientific Instrument account, General Fund	48,407	8	2
Do. K. K. Tagore Fund	25,000	0	0
Botanical Instrument account	2,329	6	0
Library account	27,351	3	4
Tools and Implements account	197	15	8
Workshop Instruments account	9,614	14	3
Sir Richard Temple Prize Fund	245	0	0
Post Office Savings Bank account	1,258	0	0
Suspense account	100	0	0
Floating Balance in the Imperial Bank, on 31st December, 1925	8,592	2	5
Cash in Office on 31st December, 1925	150	12	0
	4,74,949	15	9

Certified that the accounts for the year 1925 have been audited and found correct.

I. C. Bose,
Honorary Auditor.

Cr.

the 31st December 1925.

	Rs.	A.	P.
General Fund	4,02,204	5	8
Ripon Prof. Fund	10,830	10	10
The Maharajah of Cooch-Behar Prof. Fund	21,510	0	0
Hare Professorship Fund	1,025	0	0
Victoria Professorship Fund	1,000	0	0
Dr. Sircar Memorial Fund	11,580	4	8
Vizianagram Fund	790	0	0
Trivandrum Donation account	600	0	0
Provident Fund account	1,323	4	7
Deposit account	476	14	0
Medal Fund (Wood burn)	500	0	0
(Dr. Sircar)	3,000	0	0
(Joykissen)	9,339	0	0
Prize Fund (Nikunja Garabini)	500	0	0
(Jatindra Chandra)	550	0	0
Interest account (Dr. Sircar Medal Fund)	735	0	0
(Ripon Prof. Fund)	6,283	14	8
(Nikunja Garabini P. Fund)	230	12	2
(Woodburn Medal Fund)	141	8	0
(Jatindra Chandra P. Fund)	135	3	0
Government of India Grant account	2,244	14	8
	4,74,949	15	9

C. V. RAMAN,
Honorary Secretary.

7. The Molecular Scattering of Light at the Critical State

BY

MANINDRA NATH MITRA, M.A.

Presidency College, Calcutta.

The object of the present paper is to point out several errors in a recent paper by K. C. Kar[1] on the scattering of light by fluids in the neighbourhood of the critical stage and to show that these errors entirely vitiate his conclusions.

The expression proposed by Kar[1] for the scattering power of a fluid at the critical temperature is

$$a_{c,r} = \frac{\pi^2}{18} \cdot \frac{(\mu^2-1)^2(\mu^2+2)^2}{\lambda^4} \cdot \frac{6^{\frac{2}{3}} . \Theta^{\frac{1}{2}}}{\left[\frac{\partial^2}{\partial v^2}\left(\frac{1}{\beta v}\right)\right]^{\frac{1}{3}}}$$

where μ is the refractive index.

Θ is the product of the Boltzman constant and the absolute temperature.

λ is the wave-length.

β is the compressibility.

$a_{c,r}$ is the fraction of light scattered near the critical state.

Kar believes that his formula for scattering is supported by the experimental data obtained in an investigation of D. K. Bhattacharya[2] on carbon di-oxide, who gets $a_{c,r} = 10{\cdot}34 \times 10^{-4}$ The supposed agreement with Bhattacharya's value is however due to a mistake in arithmetical calculation. Taking the values he has used for the constants, *i.e.*,

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[1] K. C. Kar, Physik-Zeitschr, Vol. XXVII, 389, 1926.

[2] D. K. Bhattacharya, Proc. Ind. Assoc. for Cult. Sci., Vol. 8, 277, 1923.

putting $p = 5400\text{Å}$

$$\odot = 1 \cdot 05 \times 10^{-16} \times 304 \cdot 35$$

$$\mu^2 = 1 \cdot 285$$

$$\left[\frac{\partial^2}{\partial v^2} \left(\frac{1}{\beta v} \right)_\lambda \right]^{\frac{1}{2}} = 20 \cdot 1 \times 10^4$$

The result comes out to be $16{\cdot}7 \times 10^4$ and not $16{\cdot}7 \times 10^{-4}$ as he has put down. The result thus found seems to be erroneous.

Again in the formula proposed by Kar, the scattering co-efficient at the critical temperature is proportional to the inverse fourth power of λ whereas in Ornstein and Zernike's[1] equation the scattering at the critical state is proportional to the inverse square of λ. Bhattacharya[2] has proved experimentally that λ^{-2} law holds in the immediate vicinity of the critical temperature and that λ^{-4} law holds only for temperatures removed from the critical state. Other workers in the field such as Andant,[3] Raman and Ramanathan,[4] testify to the truth of λ^{-2} law at the critical state. Mr. Kar's formula has thus no relation to the actual facts.

The grounds on which Kar criticises the work of Ornstein and Zernike are also not substantial.

Ornstein and Zernike's equation for scattering per unit volume per unit solid angle and in a direction perpendicular to the incident beam is

$$a = \frac{2\pi^2 \frac{R\tau}{N} v\mu^2 \left(\frac{\partial \mu}{\partial v} \right)^2 \lambda^{-4}}{-\frac{\delta p}{\delta v} + 4\pi^2 \frac{R\tau}{v^2} \left(\frac{\epsilon}{\mu\lambda} \right)^2}$$

---

[1] Ornstein and Zernike, Proc. Amsterd, Akad. 17, 793, 1915.

[2] D. K. Bhattacharya, Proc. Ind. Assoc. for Cult. Sci., 8, 277, 1923.

[3] Andant, Comptes Rendus, p. 170, June 28, 1923.

[4] Raman and Ramanathan, Proc. Roy. Soc. A., Vol. 104, 1923.

The denominator of the equation contain two quantities

$$(1) -\frac{\delta p}{\delta v} \quad \text{and} \quad (2)\ 4\pi^2 \frac{R\tau}{v^2}\left(\frac{\epsilon}{\mu\lambda}\right)^2.$$

In the above expression—

R is the gas constant.

v is the molecular volume.

N is the Avogadro number.

τ is the absolute temperature.

ϵ is the range of the radius of action of a single molecule.

If the values of $-\frac{\delta p}{\delta v}$ as known from determinations of compressibility and those of

$$4\pi^2 \frac{R\tau}{v^2}\left(\frac{\epsilon}{\mu\lambda}\right)^2$$

as determined from the observation of the maximum opalescence at the critical temperature, are written for various temperatures, it is clear as shown in the accompanying table, that at 31·35°C, the critical temperature of carbon di-oxide, $\frac{dp}{dv}$ becomes equal to 0 and its values very rapidly increase as the temperature is lowered. On the other hand the value of

$$4\pi^2 \frac{R\tau}{v^2}\left(\frac{\epsilon}{\mu\lambda}\right)^2$$

in the liquid at temperatures a few degrees below the critical temperature increases very slowly in comparison and become quite negligible in comparison with the value $\frac{dp}{dv}$ in the liquid at a few degrees below the critical temperature. Mr. Kar's contention that the Ornstein-Zernike's formula does not reduce to the Einstein formula for liquids at ordinary temperatures is thus seen to be without foundation.

TABLE I.

Putting $A = -\frac{\delta p}{\delta v}$ and $B = \frac{4\pi^2 R\tau\epsilon^2}{v^2\mu^2\lambda^2}$

Temp.	A	B
31°C	$5 \cdot 495 \times 10^4$	$2 \cdot 376 \times 10^4$
30°C	$20 \cdot 61 \times 10^4$	$2 \cdot 875 \times 10^4$
29°C	$36 \cdot 20 \times 10^4$	$3 \cdot 135 \times 10^4$
27°C	$100 \cdot 2 \times 10^4$	$3 \cdot 473 \times 10^4$
25°C	$177 \cdot 8 \times 10^4$	$3 \cdot 802 \times 10^4$
20°C	$388 \cdot 2 \times 10^4$	$4 \cdot 248 \times 10^4$
15°C	$695 \cdot 8 \times 10^4$	$4 \cdot 625 \times 10^4$
10C	1042×10^4	$4 \cdot 941 \times 10^4$
5C	1903×10^4	$5 \cdot 144 \times 10^4$

Mr. Kar has also questioned the correctness of the method used by Ornstein and Zernike in their theoretical investigation. With regard to this, it may be pointed out, the physical conditions prevailing in the neighbourhood of the critical state are such that one may reasonably expect that the scattering co-efficient will be proportional to λ^{-2} as actually found in experiment and not λ^{-4}. For, the scattering units at this stage are not individual molecules but comparatively large clusters of molecules.

It is well known that the intensity of light scattering by units not very small in size is governed by the λ^{-2} law.

Indeed one may conclude from the observations that critical opalescence is due to the light scattered by innumerable irregular surfaces bounding the clusters of molecules.

The author's thanks are due to Prof. C. V. Raman for the facilities he gave me in using the library of the Science Association.

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8. A Study of the Acoustics of the Stroh Violin

By

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§ 1. INTRODUCTION.

The ordinary violin is a very good instrument from a musical point of view. But to physicists it is a very complicated instrument; there are four strings passing over the bridge supported on one side by the soundpost. The belly consists of curved plates of wood having two *f* holes, and enclosing an air chamber of complicated shape. Thus the reactions of the strings, the assymetrical nature of the constrained motion of the bridge imposed by the sound post, and the multiple resonance of the belly and the bridge, are physical complications. Further, the geometrical connections between the different parts are not definitely known. In spite of these complications considerable progress has been made in interpreting the acoustics of the violin, and the mechanics of bowing as influenced by the instrument. The mechanical theory[1] given by Professor Raman, takes into consideration the vibration of the bridge and the belly, and concludes that a large bowing pressure is required at the resonance frequencies, and that when the pressure falls below a certain limit the sound alternately waxes and wanes. The theory has been tested in a general way in the case of the ordinary violin with the help of the mechanical violin player[2] devised by Prof. Raman, but there is no complete verification of the theory; hence an instrument consisting of simple mechanical systems has been selected for the above purpose. This instrument is the Stroh violin. It is musically not much inferior to the ordinary violin, but far less complicated in its make, and the geometrical connections between the parts are calculated easily. In the present paper an account is given of the complete study of the acoustics of the Stroh violin with a view to verify the mechanical theory.

[1] Bulletin No. 15, Indian Assn., Calcutta, 1918.

[2] Proc. Ind. Assn., Calcutta, Vol. 6, p. 19 (1920).

§2.

DESCRIPTION OF THE STROH VIOLIN.

The Stroh violin consists chiefly of five parts—(*i*) the body, (*ii*) the string, (*iii*) the bridge, (*iv*) the diaphragm, and (*v*) the horn. The complete instrument is shown in Fig. 1, and Fig. 2, in Plate VIII shows the same without the horn. The body consists of a solid block of wood of the shape shown in Figs. 1 and 2. The upper part of the body is more or less similar to that of the ordinary violin, and as usual with all stringed instruments there is one tightening screw, the ear at the top. At the lower end of the solid block a hole is drilled transversely to allow the bridge to pass through it, and there is a circular hole sideways, to keep the diaphragm in position, as shown in Fig. 2. The vibrating string is one steel wire, one end of of which is fixed to a hook at the lower end of the body, and the other end is attached to the tightening screw for adjustment of tension. The length of the wire is about 63 cm. and its diameter is about ·76 mm. and it has a mass of ·035 gms. per cm. The vibrations are produced by the bow applied near the bridge and the pitch is altered by varying the vibrating lengths. The range of frequencies that can be obtained from the instrument is from 200 to 800 vibrations per second; shorter lengths hardly produce any sound. By varying the tension, however, the range can be controlled. The string passes over the bridge at the lower end as shown in Fig. 2. The bridge is a rectangular brass piece 2·5 mm. thickness, and its breadth in the plane of vibration varies from 4·78 mm. to 2·5 mm. at the end joined to the diaphragm. The upper part supports the taut wire. Fig. 3 shows the bridge and the diaphragm; a part of the horn is also sketched there. This part is cylindrical. The is pivoted between two conical steel bearings; the connection between the bridge

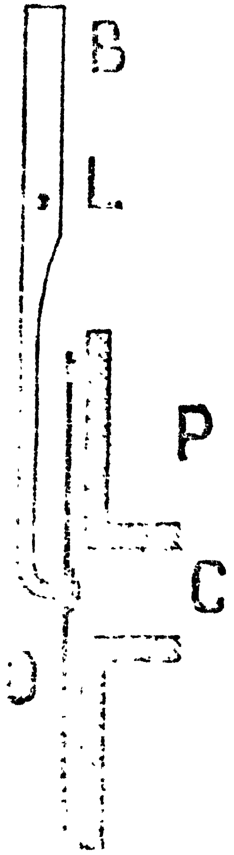

FIG. 3

and the diaphragm is made by a short rectangular bend of the bridge which is rigidly connected to the diaphragm by a tightening nut. The lengths of the two parts on either side of the bearings, are 5·1 cm. and 2·2 cm. the upper part being shorter, hence if the free end of the bridge is caused to vibrate with an amplitude of 1 mm., the other end connected to the diaphragm will move through twice that distance. The mass of the bridge is about 5 grams; the diaphragm is placed inside a circular hole scooped out of the body. A thin sheet-rubber ring is placed upon the rim of the circular diaphragm and it is clamped at the edge by a metal piece which is screwed to the body as shown in Fig. 2. This metal piece presses the diaphragm through another rubber ring. The effect of placing the rubber ring is to prevent a rattling noise. The diaphragm is connected to the bridge at the centre. The radius of the diaphragm is 2·6 cm. and it is made of steel of density 7·8, and the thickness of the plate is ·025 cm. As mentioned before, the diaphragm being in rigid connection with the lower end of the bridge, will have the same amplitude as the lower end of the bridge. Since the dimension of the bridge in the plane of vibration is large, it will hardly vibrate as a cantilever about the pivot or the fixed end. The conical bearings prevent any longitudinal motion of the bridge along the direction of the string, so that the bridge moves simply about the pivot. From Fig. 3 it will be seen that the rectangular bend of the bridge is very thin at the end connected to the diaphragm ; this has been done purposely to impart elasticity at that end. From Fig. 1 it will be seen that the horn does not end in a point, but the end is a short cylindrical piece, whose length is about 5 cm. and whose internal diameter is about 9 cm. ; the horn is a cone at the vertex of which a short cylinder is attached, and at the open end a short flange is added. The slant length measured along the generating lines from the end of the cylinder to the flange, is about 33 cm. and the diameter of the open end is 12 cm.

The mechanism of the production of sound is very simple in the present case. Its principle is the same as found in the gramophone. The vibration of the string produces a transverse force on the bridge which moves in its own plane about the pivot ; the bridge communicates a transverse motion to the diaphragm and this produces sound waves in the horn. The cylindrical attachment is made air tight by fixing it tightly over the diaphragm, and any slight leakage is stopped by ordinary vaseline.

§3.

FREE PERIODS OF THE STROH VIOLIN.

(*a*) *Theory.*

From the description of the instrument given above it will be found that the parts capable of free vibration are (1) the string, (2) the bridge, (3) the diaphragm, and (4) the horn. Out of these the string vibrations are the most important ones. The free vibrations of the string fixed at two ends, are given by

$$pl = m\pi \tag{1}$$

where $p = 2\pi/$wave length, and m is an integer.

It has been mentioned above that the breadth of the bridge is very large in the plane of vibration. Hence the free vibrations of the bridge about the pivot or the clamped end, will have a high frequency, and too small an amplitude to be taken into consideration. There may be slight longitudinal motion along the direction of the string in the short portion of the bridge; but this sort of vibration will not produce any vibration in the diaphragm. Hence we find the elastic vibrations of the bridge are of little importance in the production of musical tone. The vibration of the diaphragm will be approximately similar to that of a supported plate with the additional load of the bridge fixed at the centre. The bridge will perform angular oscillations about the pivot due to the motion of the centre of the diaphragm. The effect of fixing the bridge at the centre will be (1) to increase the effective inertia of the diaphragm, and (2) to prevent the excitation of the diametral modes of vibration. The free periods of a supported plate can be calculated on the basis of the simple theory given by Prof. Lamb[3] in the case of the clamped plate, and that given by Prof. Prescott[3a] for supported plate. Let the motion of the diaphragm be of the prescribed type

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[3] Proc. Roy. Soc., sec A., Vol. 98, p. 205 (1921).

$$y=\mathrm{A}\cos pt\left(1-\frac{r^2}{a^2}\right)$$

(supported edge), whose r is the radial distance of the vibrating point, and a the radius of the diaphragm. It will be seen that the prescribed condition satisfies the condition of no displacement at the edge. Taking into consideration the effective inertia of the bridge, and the additional kinetic energy due to it we have for V, the potential energy

$$\mathrm{V}=\frac{\mathrm{E}h^3}{24(1-\mu^2)}\iint\left(\frac{1}{\mathrm{R}_1^2}+\frac{2\mu}{\mathrm{R}_1\mathrm{R}_2}+\frac{1}{\mathrm{R}_2^2}\right)d\mathrm{S}$$

where $d\mathrm{S}$ is an element of area and R_1^{-1}, R_2^{-1}, are the principal curvatures.

$$\mathrm{R}_1^{-1}=\frac{d^2y}{dr^2}\text{, and }\mathrm{R}_2^{-1}=\frac{1}{r}\frac{dy}{dr},\quad d\mathrm{S}=2\pi r\,dr$$

On evaluation

$$\mathrm{V}=\frac{\mathrm{E}h^3\pi c^2}{3(1-\mu)a^2}$$

$$c=\mathrm{A}\cos pt.$$

$$\mathrm{T}=\frac{\pi\rho_1 ha^2\dot{c}^2}{6}+\tfrac{1}{2}\mathrm{M}\dot{c}^2$$

where M=mass of bridge ; $\rho_1=7\cdot 8$ $\mu=\frac{1}{4}$

$$p/2\pi/=10^5.\frac{p.1\cdot 33^*}{a^2}\Big/\left(1+\frac{3\mathrm{M}}{m}\right)^{\frac{1}{2}}\quad[\mathrm{E}=2\times 10^{12}]\quad\ldots\quad(2)$$

[3a] Applied Elasticity, p. 598, Art 387. Longman's (1924).

[*] In the more accurate formula given by Prescott, the numerical factor is 1·2 instead of 1·33.

m=mass of diaphragm

Effective mass $M=1\cdot3$ grms.

and $m=4\cdot6$ grms.

$a=2\cdot6$ cm. (radius of diaphragm)

$h=.025$ cm. (thickness)

$$\frac{p}{2\pi}=370 \qquad \ldots \quad (3)$$

For a clamped plate

$$p/2\pi/=2\cdot5\times10^{5}\frac{h}{a^{2}}\Big/\left(1+\frac{5M}{m}\right)^{\frac{1}{2}} \qquad \ldots \quad (2a)$$

$$p/2\pi/=564$$

The prescribed mode of vibration assumed in the case of a supported plate, makes y zero at the rim, but makes the bending moment constant across every section of the plate. It is therefore very far from satisfying the boundary condition that the bending moment across the rim is zero, but it will do to make a rough calculation of the free period of the plate clamped by rubber rings, which certainly do not clamp rigidly as contemplated in equation (2a).

The diaphragm communicates vibration to the horn which can be treated as a cone. Neglecting the slight flange, and treating the vertex to be closed, and the other end to be open the natural frequency will be given by

$$\frac{p_{2}}{2\pi}=q.\frac{v}{2l} \qquad \ldots \quad (4)$$

where q is an integer, v=velocity of sound in air, and l=slant length

$v=340$m. $l=33$

$p_{2}/2\pi=q.\ 510.$

(*b*) *Experimental determination of the free periods of the Stroh violin.*

No attempt was made to determine the free period of the string very accurately, and find out the effect on the period of the coupled oscillation of the diaphragm. The determination of the free period of the diaphragm and the horn was made in the following way.

It is well known that stringed instruments refuse to produce a steady tone at a certain pitch, and a beating tone is produced, and at this pitch the body of the instrument is thrown into vigorous vibration.[4] This pitch is known as the wolf-note pitch. At this pitch the vibration of the string when played pizzicato, dies out very rapidly. Two methods were therefore adopted, (1) by plucking and observing the duration of vibration of the string visually, and (2) by bowing and finding out the wolf-note pitch. In method (1) it was found that the vibrations last long at low frequencies, then as the pitch is raised by coming down the string, a point is reached where the duration becomes very short and the loudness of the sound produced increases considerably; as we go further down, a second point is reached when the intensity rises and a slight change in the duration of vibration is observed. Similarly a third point is reached at very high frequency. The horn is then removed and the experiment repeated, now the second point does not show any increase in the loudness. It may be mentioned here, that on removing the horn, there is a general diminution of the intensity, hence the plucking should be started from low frequency, and the length of the string should be quickly altered in order to be able to detect the change in the intensity and the duration of vibration. It is clear that the second point is the resonance pitch of the horn.

The method of bowing the string and altering the length quickly, at once shows rise of intensity at the three points mentioned above. And as soon as the horn is removed the second point vanishes. At the first and the third points a beating tone is produced, and beating persists even when

[4] Helmholtz, Sensations of Tone, p. 85, also Phil. Mag., Vol. 33, p. 392 (1916)

the horn is removed. It is very easy to find out that the bridge vibrates vigorously at the first and the third point by putting the finger lightly on the bridge. By putting a mirror on the bridge and reflecting a spot of light on the screen, it is visually observed that the amplitude increases enormously at the first resonance and that there is a definite rise at the third point. At the second point, no beating tone is produced, and the bridge does not show any increase in the amplitude of vibration. Hence it is concluded that the first and the third resonances belong to the diaphragm, while the second one is due to the horn. The frequencies of the three were found by comparison with a standardised sonometer. The results show the following agreements.

Freq. cal.	Freq. obs.
Diaphragm	
370	380
...	760
Horn	
510	497

The discrepancy between the observed and calculated values of the frequency of the diaphragm is due to the nature of the clamping at the rim. On account of the presence of the rubber rings the edge cannot be regarded as a rigidly fixed boundary for which the calculated frequency comes out to be 561, while it cannot be truly a supported edge; Prof. D. C. Miller[5] has remarked in his book that the frequency of a circular diaphragm depends greatly upon the nature of clamping at the edge, for instance, the frequency changed from 640 to 916 on clamping tightly.

During these experiments it was also observed that at the first and the third point, the beating tone gives place to a steady tone on increasing the bowing pressure. Also the beating tone becomes more pronounced when the bow is closer to the bridge, vanishing when the bow is removed further from the bridge. With all possible efforts, *i.e.*, by decreasing the pressure, or by removing the bow very close to the bow, or doing the reverse, the beating tone could not be produced at the second resonance which is due to the horn.

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[5] Science of Musical Sounds, p. 151 (Macmillan).

The tension of the wire was changed, and all the above experiments were repeated, but it was found that the frequencies of the resonance points were always the same. So that we now establish that the Stroh violin has three resonance frequencies two of which represent the diaphragm resonance, and one the horn resonance. The first is the strongest of the three. The amplitude of vibration of the diaphragm measured at the first resonance, came up to $\cdot 456 \times 10^{-2}$ c.m. while at other points it ranged between $\cdot 11 \times 10^{-2}$ to $\cdot 71 \times 10^{-3}$ c.m. When the bridge was loaded further, it was found that the resonance pitch of the diaphragm shifted towards lower frequency, while the horn resonance remained in its original position. The following table shows the effect of the load :[6]

TABLE (1)

Load.	Freq. obs.
0	380
1 grm.	325
2 grms.	313

§ 4.

STUDY OF THE FREE VIBRATIONS OF THE STRING AND THE BRIDGE.

(*a*) *Experimental determination of the damping co-efficient.*

In the present section an account is given of the experiments on the free vibrations of the string and the bridge as coupled together, and the theory is developed and compared with the experimental results. When a string whose two ends are absolutely fixed is caused to oscillate by plucking, the vibrations last for a long time, and the rate of decay of vibrations is very small, and it is independent of the frequency of vibration; the slow rate of decay is due to the small loss of energy by friction against air. But the case is otherwise when the string is connected to another body capable of vibration and radiation. In the present case such a system is the bridge and the diaphragm. The damping of the diaphragm will be the sum of the damping due to (1) the friction between the bearings and the bridge, and (2) that due to loss of energy by radiation of sound in free space. The damping of the string will depend upon the amplitude of vibration of the bridge. When the amplitude of vibration of the bridge is large, energy is rapidly drawn from the string, hence the vibration of the latter dies out quickly. So that the rate of decay of vibration of the string depends upon the nearness of the frequency of vibration of the string to the natural frequency of the diaphragm when the amplitude of the latter increases enormously.

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[6] Phil. Mag., Vol. 35, p. 493 (1918).

The damping coefficient of the string was determined by photographing the transverse vibration of the string after plucking. The frequency was varied by altering the vibrating lengths, and the plucking point which coincided with the bowing region, was kept constant. The vibration was photographed in the following way: From Fig. 2 it will be seen that there is sufficient space between the string and the wooden body near the bowing region. To photograph the vibrations of the string the instrument was kept vertical, and it was rigidly fixed, so that there was no irregular movement of the body during plucking. Light was thrown from the left side of the instrument upon a small mirror fixed to the body near the bowing region, and inclined to the body at an angle of 45° so that light after reflection passed through the vibrating wire and travelled in a horizontal direction. A fine slit was placed very close to the wire so that the slit, when focussed by a lens, gave a white line, crossed by the shadow of the string, which was a black point. When the string vibrated, the black dot when photographed on a vertically falling plate, gave a damped wavy curve on a white background. The frequencies at different lengths were obtained by comparison with the sonometer. In one plate four or five photographs were taken for the same length of the vibrating wire. The damping coefficient was determined by measuring the ordinates after ten or twelve vibrations. Since the frequency was known, the damping coefficient could be determined from the formula

$$K_1 = 2{\cdot}3 \log_1 \frac{AN}{A_0 n} \qquad (5)$$

where A_0=initial amplitude, and A the same after n vibrations, N=frequency. The mean of five sets of observations was taken and the result tabulated below.

TABLE (2)

$T_0 = 1{\cdot}7 \times 10^6$ dynes.

Freq.	600	568	500	480	441	420	380	343	330	320	248
$K \times 10^{-2}$	·90	·61	·80	·40	·35	1·32	3·10	1·23	·25	·23	·25

It is found that the damping coefficient of the string increases about ten times near the region where the frequency of the string and the diaphragm coincides, and there is a slight increase near the horn resonance. At low frequencies the damping coefficient tends to a limiting value $\cdot 24 \times 10^2$ while at high frequencies there is a definite tendency of the coefficient to rise with pitch.

(*b*) *Free vibration of string and bridge without damping.*

Theoretically the free vibration of the string and the bridge as coupled together can be found easily when the damping of the former is neglected.

If the vibration of the string be assumed to be of the type

$$y = A \sin px . \cos mt$$

then the transverse force on the bridge is given by

$$-T_0\, p\, A \cos pl \cos mt.$$

There will be a small longitudinal force tending to displace the bridge along the direction of the string which, as explained in sec. (2), can be neglected. Let the kinetic energy of the system consisting of the diaphragm and the horn be represented by

$$T = \tfrac{1}{2}M_1 \dot{\phi}_1^2 + \tfrac{1}{2}M_2 \dot{\phi}_2^2 + \ldots$$

$$V = \tfrac{1}{2}M_1 n_1^2 \phi_1^2 + \tfrac{1}{2}M_2 n_2^2 \phi_2^2 + \ldots$$

where ϕ_1, ϕ_2 etc. are normal co-ordinates, M_1, M_2 are the inertia, and $\frac{n_1}{2\pi}$ $\frac{n_2}{2\pi}$ are the natural frequencies of the bridge, and the horn. The transverse component of the motion of the bridge is

$$A \sin pl \cos mt. = \gamma_1 \phi_1 + \gamma_2 \phi_2 + \ldots \qquad \text{etc.} \quad (6)$$

and the magnitudes of ϕ_1, ϕ_2 can be obtained from the forced vibrations

$$\ddot{\phi}_1 + n_1^2 \phi_1 = \Phi_1 / M_1$$

$$\ddot{\phi}_2 + n_2^2 \phi_2 = \Phi_2 / M_2$$

where Φ_1, Φ_2, are the generalised components of force, and are equal to

$$\left.\begin{aligned} \Phi_1 &= \gamma_1 T_0 p\, A \cos pl \cos mt \\ \Phi_2 &= \gamma_2 T_0 p\, A \cos pl \cos mt \end{aligned}\right\} (7)$$

Substituting these values in (6), we obtain the following relation

$$\tan pl = T_0 p \left[\frac{\gamma_1^2}{M_1(n_1^2 - m^2)} + \frac{\gamma_2^2}{M_2(n_2^2 - m^2)} + \right] \tag{8}$$

This may be interpreted as the equation showing the effect on the natural frequency of oscillation of the yielding of the bridge. The effect is greater the nearer is m to n_1, n_2 etc. and becomes maximum when $n_1 = m$, or $n_2 = m$, *i.e.*, when the frequency of the bridge coincides with that of the string. Equation (8) can be solved graphically.[7] The curves are similar to those given by Morton & Chambers[8] in the case of the coupled oscillation of bar and string.

(c) *Free vibration of spring and bridge with damping.*

Confining attention to the first resonant vibration of the diaphragm, we shall assume that the free vibrations of the string are of damped type. Let it be represented by

$$y = F \left[e^{(ip+q)(x+a_1 t)} - e^{-(ip+q)(x-a_1 t)} \right] \tag{9}$$

At the point $x = l$ where the string passes over the bridge, the equation of motion of the latter takes the form

$$M_1 \frac{d^2 y}{dt^2} = -T_0 \frac{dy}{dx} - f^2 y - g^2 \frac{dy}{dt} \tag{10}$$

T_0 = tension.
M_1 = mass of bridge.
f = restoring force.
g^2 = friction coefficient.

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[7] Bulletin No. 15, Indn. Assn., Calcutta, p. 122.
[8] Phil. Mag. Vol. 50, p. 570 (1925).

From (9) and (10), after substituting the value of $\frac{dy}{dx}$ at $x=l$, we get after simplification[9]

$$\tan pl = -\frac{T_0p+Bql}{A-T_0q^2l} = \frac{Aql+T_0q}{B+T_0pql} \qquad (11)$$

where $A=M_1\left[(n_1^2-m^2)+q^2a_1^2+kaq\right]$

and $B=M_1m\left[2a_1q+k\right]$

$n_1^2=f^2/M_1,\quad m=pa$ and $k=\frac{g^2}{M}$

From (11) qa_1, can be determined by cross multiplication. But it is found that the equation in qa_1 is of fifth order. The coefficients of higher powers are however small within the range of frequencies for which qa_1 has been determined. Hence neglecting them, we get

$$qa_1 = -\frac{k}{\left[\frac{Mm\pi}{\rho a_1}(\gamma^2-1)^2+1+\gamma^2\right]} \qquad (12)$$

$\gamma=n/m$. From (11) we find that the rate of decay of the free vibrations of the string has little influence on the period of vibration of the string since the terms containing q are small, but the effect of the vibrations of the bridge on the free period of the string is the same as pointed out before. Equation (12) shows the effect of the vibration of the diaphragm on the rate of decay of vibration of the string. K, it will be remembered, is the sum of the damping due to friction and that due to radiation of sound. Lamb has calculated the damping coefficient of a telephone plate due to radiation alone[10]

$$2k_1 := \frac{5}{36}\,\frac{\rho}{\rho_1}\,\frac{n_1^2a^2}{hv}$$

ρ_1 = density of plate.
ρ = density of medium, and v = velocity.
a = radius of the plate.
h = thickness.

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[9] Bulletin 15, Indn. Assn., Calcutta, p. 128.

[10] Loc. cit (3).

For an iron plate of the same dimensions as the diaphragm of the Stroh violin

$$k_1 = 6{\cdot}9$$

This is found to be very small in comparison to the damping due to friction between the pivots, which is of the order 10^2. Hence though k involves a part which varies with pitch, it can be neglected, and the damping coefficient k in equation (12) can be regarded as constant. (12) shows that the rate of decay of vibrations of the string will be maximum when $n_1 = m$, *i.e.*, when the free period of the string coincides with that of the diaphragm. It is then equal to $+\frac{K}{2}$. At other frequencies it is given by

$$qa_1 = \frac{8{\cdot}8 \times 10^2}{[2{\cdot}06 \times 10.^{-2} m(\gamma^2 - 1)^2 + 1 + \gamma^2]} \quad *$$

TABLE (3)

Freq.	200	250	300	350	380	400	500	570	650	700	800
qa_1	1·9	8·0	2 × 10^1	1·1 × 10^2	4·4 × 10^2	2·0 × 10^2	3·7 × 10^1	2·6 × 10^1	1·3 × 10^1	1·0 × 10^1	5·2

On comparison it will be found that the calculated values agree fairly with the experimental ones. The maximum at the resonance point of the horn is not brought about, this is due to the fact that we have neglected other resonance frequencies n_2, n_3 etc, which will give us terms similar to (12). The general feature of the variation of the damping coefficient is found to be the same in both the cases. The rise of damping coefficient at high frequencies is probably due to high resonance frequencies not taken into consideration. The calculated values show a tendency to a limiting value at low frequencies as observed experimentally.

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* Dimensions same as before.

§ 5.

MECHANICS OF BOWING.

(a) *Kinematics of the string.*

From the kinematics of the bowed string it has been deduced that the velocity of the bowed point has one constant velocity during the forward motion when it is dragged with the bow, and this velocity of the string is very nearly equal to that of the bow, while in the back-ward motion, the velocity of descent is also constant in the normal Helmholtzian type of vibration, and it is much larger than the forward motion. The velocity of descent v is related as follows

$$\frac{V_0}{V_0+v}=\frac{x_0}{l}$$

V_0 = velocity of bow.
x_0 = distance of bowed point from the bridge.

And the intervals during which the point moves with velocity V_0 and v are given by

$$\frac{V_0}{v}=\frac{x_0}{l-x_0}$$

The frictional force exerted by the bow depends upon the velocity of the point relative to the bow, and since the velocity is constant, the frictional force is also constant during the two intervals. The frictional force in the forward motion is greater than in the downward motion, since the coefficient of friction between two unlubricated solids is greater the smaller the relative velocity between the two bodies in contact. In fact with these premises, the dynamical principles of bowing can be worked out. Let us suppose that the velocity of the bow is V_0 and that the velocity of the bowed point be given by

$$\dot{y}=\dot{\psi}_1 u_1+\dot{\psi}_2 u_2+ \quad \dots \qquad (13)$$

where ψ_1, ψ_2 are normal co-ordinates, u_1, u_2 etc. are normal functions for the string. The equations of the forced vibration are of the form

$$a_1\dot{\psi}_1+b_1\dot{\psi}_1+c_1\psi_1=\mathrm{F}\,u_1 \tag{14}$$

where F is the frictional force between the bow and the string. Assuming that the relative velocity $(\mathrm{V}_0-\dot{y})$ does not become zero or change sign we may expand F in a form

$$\mathrm{F}=\mathrm{F}_0(\mathrm{P})+\mathrm{F}_1(\mathrm{P})(\mathrm{V}_0-\dot{y})+\mathrm{F}_2(\mathrm{P})(\mathrm{V}_0-\dot{y})^2 \tag{15}$$

where F_0 (P), F_1 (P) etc. are functions of pressure. Substitute the value of $\dot{y}$ from (13) in (15) and then replace F in (14) by the series derived by expansion (15). The terms on the right hand of (14) will then represent periodic forces of various frequencies. Confining attention to the first power of the relative velocity, and retaining the term which has the same frequency as the normal co-ordinate we obtain the force as given by

$$-\mathrm{F}_1(\mathrm{P})u_1^2\dot{\psi}_1 \tag{16}$$

Then (14) reduces to the form

$$a_1\ddot{\psi}_1+\{b+\mathrm{F}_1(\mathrm{P})u_1^2\}\dot{\psi}_1+c_1\psi_1=0 \tag{17}$$

Since the dynamic co-efficient is less than the static one, therefore F_1 (P) is negative. Now by increasing the pressure the magnitude of F_1 (P) can be increased; hence by applying pressure, the second term in (17) can always be made negative; the solution then shows that ψ_1 continually increases with time exponentially, and similarly other normal co-ordinates will behave in the same way. The inference is that when the bow is applied with sufficient pressure the vibration of the point will continue to increase until the limits of validity of (15) are reached, that is, until the velocity of the bowed point is the same as that of the bow, beyond which point no further increase of the maintained motion occurs.

(b) *Bowing pressure at different pitches.*

The experimental study of the bowing pressure to elicit a steady tone, has been made with the mechanical violin player.[11] The Stroh violin is made to travel backward and forward on well oiled rails by a cycle chain and its free wheel gear. The chain is provided with a small pin which moves up and down in a slot which is fixed to the base upon which the instrument rests. when the chain is revolved by a motor or hand wheel the pin in one journey rests at the top of the slot and in its return journey it goes down. The bow is fixed to a wooden lath which is hinged to a cycle hub so that a short arm projects beyond the hub on one side, and the whole works like a steel yard. The bow is counterbalanced by weights hung on the short arm, and the bowing pressure is adjusted by placing weights at a particular point of the lath, also by using riders. For smooth working of the bow, a few circular disks are fixed horizontally on a stout wire which is hung on the short arm inside water or oil. In this way approximately the conditions of the violin player are realised. The minimum pressure to elicit a steady tone was found in every case. The pitch was altered by changing the vibrating lengths of the string. In order to imitate the finger of the violin player a piece of rubber pressed against the string, and it was firmly clamped. The bow was kept at a constant distance about 8 cm. from the bridge, the place generally selected by the musicians for bowing. The frequencies were determined by comparison with a standardised sonometer. The table below gives the mean results of the experiments. Bowing pressure was calculated from the position and mass of the load attached to the lath, and at every pitch bowing was started from the smallest load. The speed of bowing was kept constant at about 30 centimeters per second the wheel being worked by a motor.

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[11] *loc. cit* (2).

TABLE (4).

Freq.	223	250	280	336	374	426	446	490	562	701
Bowing pressure in grammes.	11	12	17·5	27	48	20	15	18	10	8

It will be observed from the above table that the bowing pressure rises considerably at the reasonance of the diaphragm, and also near the horn resonance, while at low frequencies, the bowing pressure was slightly greater than at high frequencies. Further it was observed that at the diaphragm resonance, when the pressure was smaller than given in the above table, a beating tone was produced which on increasing the pressure vanished and gave place to a steady tone. Bowing pressure also increases when the bowed point is brought closer to the bridge. It also increases with the speed.

(c) *General explanation of bowing pressure and its theory.*

The general explanation of the increase of bowing pressure, and the production of a beating tone, has been given by Prof. Raman. "In the particular case in which the frequency of free oscillation of the string coincides with that of the diaphragm, the mode of vibration of the string is initially of the well-known type in which the fundamental is dominant. But the vibrations of the string excite those of the diaphragm, and as the vibrations of the latter increase in amplitude, the rate of dissipation of energy increases continually till it outstrips the critical limit beyond which the bow fails to maintain the usual type of vibration. As a result of this, the mode of vibration of the string progressively alters to a type in which the fundamental is subordinate to the octave in importance. The vibrations of the diaphragm then decrease in amplitude, but as may be expected, this follows the change in the vibrational form of the string by a considerable interval. The decrease in the vibration of the diaphragm results in a falling off of the rate of dissipation of energy, and when this is again below the critical limit the string regains its original form of vibration, passing successively through similar stages but in the reverse order. This is then followed by an increase in the vibration of the diaphragm, and the cycle repeats itself indefinitely."[12] If the pressure be increased so that the rate of dissipation even with resonance vibrations of the diaphragm, is below the energy supplied by the bow, then a steady tone is produced, hence at the resonance vibrations, the pressure must be increased to produce a steady tone. At the horn resonance we have seen that no beating tone is produced, but there is rise of bowing pressure, this is again due to the increase in the rate of dissipation of energy. The reason why no beating tone is produced, is that even with resonance and large vibration, the dissipation is not so great that the bow at that particularal pressure is incapable of maintaining the vibration of the fundamental. It is only in those cases where the minimum pressure of the bow is very much smaller than the pressure required to maintain the vibration of the fundamental only, and at the same time is greater than the pressure required to maintain the vibration of the octave, that we obtain the beating tone, and the change in the form of vibration as shown in fig. (4). Even in the case of resonant vibration of the diaphragm the beating tone disappears when the bow is removed further away from the bridge, for then the above conditions are not satisfied. While in the case of horn resonance the above conditions are not realised even by taking the bow closer to the bridge.

The quantitative estimation of the bowing pressure will now be given. The first step is to obtain the magnitude of the force applied in terms of the amplitude of vibration of the string, and the vibration of the bridge.

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[12] Phil. Mag., Vol. 33, p. 392 (1916).

(*d*) *Forced vibration of the string and bridge.*

Let $E_1 \cos mt + E_2 \sin mt$ be the periodic force acting at $x = x_0$ of the string. The vibration of the string on the two sides of the point at which the force acts, will be given by

$$y = A \sin px \cos mt + B \sin px \sin mt \text{ if } 0 < x < x_0 \text{ and}$$

$$y = C \sin p(l-x) \cos mt + D \sin p(l-x) \sin mt + G \cos p(l-x) \cos mt$$
$$+ H \cos p(l-x) \sin mt \text{ if } x_0 < x < l \qquad \dots \quad (18)$$

From the above equations the transverse force in the bridge is

$$T_0 p \, (C \cos mt + D \sin mt)$$

and the vibration of the bridge resulting thereform is

$$y = G \cos mt + H \sin mt.$$

Since the force and the resulting vibration must be proportional to each other, we must have two relations of the form

$$\left.\begin{aligned} G &= \alpha C - \beta D \\ H &= \beta C + \alpha D \end{aligned}\right\} \qquad \dots \quad (19)$$

From which on squaring and adding we find

$$G^2 + H^2 = (\alpha^2 + \beta^2)(C^2 + D^2).$$

The continuity of the displacement at $x = x_0$ gives

$$\left.\begin{aligned} A \sin px_0 - C \sin p(l-x_0) - G \cos p(l-x_0) &= 0 \\ B \sin px_0 - D \sin p(l-x_0) - H \cos p(l-x_0) &= 0 \end{aligned}\right\} \quad \dots \quad (20)$$

Since the impressed force $E_1 \cos mt + E_2 \sin mt$ is balanced by the resultant of the tensions at $x = x_0$, we have

$$\left.\begin{aligned} A \cos px_0 + C \cos p(l-x_0) - G \sin p(l-x_0) &= E_1 / T_0 p \\ B \cos px_0 + D \cos p(l-x_0) - H \sin p(l-x_0) &= E_1 / T_0 p \end{aligned}\right\} \quad \dots \quad (21)$$

Eliminating A, B, G and H from (19), (20) and (21) and solving for C and D and writing $\alpha=\tan\delta$, we get

$$C \sin pl+G \cos pl=E_1 \sin px_0/T_0 p$$

$$D \sin pl+H \cos pl=E_2 \sin px_0/T_0 p$$

from which we obtain

$$E_1^2+E_2^2=\frac{(C^2+D^2).\ T_0 p.\ \{\sin^2(pl+\delta)+\beta^2 \cos^2 pl.\ \cos^2\delta\}}{\sin^2 px_0 \cos^2\delta.}$$

$$\text{and} \quad \frac{E_1}{E_2}=\frac{C \sin(pl+\delta)-\beta.D.\ \cos pl \cos\delta}{D \sin(pl+\delta)+\beta C.\ \cos pl \cos\delta} \quad \ldots \quad (22)$$

The equations (22) give the magnitude of the force and the phase in terms of the amplitude of the string and the forced vibration of the bridge. The quantities α and β are such that

$$(\alpha^2+\beta^2)^2/T_0 p$$

measures the amplitude, and β/α the phase of the forced vibration of the bridge produced by unit force acting upon it. In the absence of dissipation $\beta=0$, and $-\alpha$ is identical with the right hand side of (8). If the form of the dissipation function be known in terms of the normal co-ordinates, the value of β and the modified value of α may be determined. As an approximation we assume that dissipation does not appreciably influence the normal modes of vibration of the bridge and the string, its effect being merely to cause the free vibrations to die with time at rates

$$e^{\frac{-k_1 t}{2}} \qquad e^{\frac{-k_2 t}{2}}$$

etc., for the respective co-ordinates. On this assumption the equation for the forced vibration of the bridge becomes

$$\left.\begin{aligned} a_1\ddot{\phi}_1+b_1\dot{\phi}_1+c_1\phi_1&=\Phi_1 \\ a_2\ddot{\phi}_2+b_2\dot{\phi}_2+c_2\phi_2&=\Phi_2 \end{aligned}\right\} \quad (23)$$

$$\text{and } \Phi_1=\gamma_1 T_0 p[\ C \cos mt+D \sin mt\ ]$$

$$\Phi_2=\gamma_2 T_0 p[\ C \cos mt+D \sin mt\ ]$$

Hence

$$\phi_1 = \frac{\gamma_1 T_0 p}{P\,a}[\,C\cos(mt-\theta_1)+D\sin(mt-\theta_1)\,] \text{ etc.}$$

$$P_1 = [\,(n_1^2-m^2)^2+k_1^2m^2\,]^{2}$$

$$\beta_1/a_1 = \tan\theta_1 = \frac{k_1 m}{n_1^2-m^2}$$

Again the transverse displacement of the bridge

$$= G\cos mt + H\sin mt$$

$$= \gamma_1\phi_1+\gamma_2\phi_2+\gamma_3\phi_3+ \quad \dots \qquad \dots \qquad \dots$$

Hence

$$G = T_0 p[\,\gamma_1^2(C\cos\theta_1+D\sin\theta_1)/P_1a_1+\gamma_2^2(\cos\theta_2+D\sin\theta_2)/P_2a_2 + \quad \dots\,]$$

$$H = T_0 p[\,\gamma_1^2(C\sin\theta_1-D\cos\theta_1)/P_1a_1+\gamma_2^2(C\sin\theta_2-D\cos\theta_2)/P_2a_2 + \quad \dots\,] \quad \dots \quad (24)$$

From (19) and (24)

$$a^2+\beta^2 = T_0^2p^2[\,\gamma_1^2/P_1a_1+\gamma_2^2/P_2a_2+ \quad \dots\,]$$

and therefore

$$\beta = T_0 p\left[\frac{\gamma_1^2}{a_1}\,\frac{k_1m}{\{(n_1^2-m^2)^2+k_1^2m^2\}}+\frac{\gamma_2^2}{a_2}\,\frac{k_2m}{\{(n_2^2-m^2)^2+k_2^2m^2\}}\right]$$

$$a = T_0 p\left[\frac{\gamma_1^2}{a_1}\,\frac{(n_1^2-m^2)}{\{(n_1^2-m^2)^2+k_1^2m^2\}}+\frac{\gamma_2^2}{a_2}\,\frac{(n_2^2-m^2)}{\{(n_2^2-m^2)^2+k_2^2m^2\}}+\right] (25)$$

If in (22) we put $pl=m\pi$ we get

$$E_1^2+E_2^2 = \frac{(C^2+D^2)\,T_0^2p^2(a^2+\beta^2)}{\sin^2 px_0}$$

$$\frac{E_1}{E_2} = \frac{aC+\beta D}{aD-\beta C} \qquad \dots \quad (26)$$

Therefore

$$\frac{\sin px_0 E_1}{T_0 p} = aC+\beta D$$

and $\frac{\sin px_0}{T_0 p}.\,E_2 = aD-\beta C$

(*e*) *Bowing pressure and pitch relations.*

If the forced vibration of the string be

$$y=\Sigma_n \sin\frac{n\pi x}{l}\left[C_n \cos\frac{2n\pi t}{T}+D_n \sin\frac{2n\pi t}{T}\right]$$

the periodic force required to maintain the vibration when the bow is applied at $x=x_0$, will be equal to

$$F=\Sigma_n \frac{T_0 n\pi/l}{\sin\frac{n\pi x_0}{l}}\left[E_{1n}\cos\frac{2n\pi t}{T}+E_{2n}\sin\frac{2n\pi t}{T}\right] \quad \ldots \quad (27)$$

E_{1n}, and E_{2n} mast be proportional to the vibration of the string, and therefore will be of the form

$$\left.\begin{aligned} E_{1n}&=\alpha C_n+\beta D_n \\ E_{2n}&=\alpha D_n-\beta C_n \end{aligned}\right\} \quad \ldots \quad (28)^{1}$$

by comparison with (26) where α and β

are given by (25). Thus we find that when the forced vibration of the bridge is very large in cases of resonance, the force required to maintain the motion is also very large. Since the force is proportional to the pressure for a given speed of bowing it follows that a large bowing pressure is required to maintain a steady motion at the resonance frequencies. Further from (27) it is found that if the bow be applied at the nodal point of a particular mode of vibration, a huge pressure will be required to elicit that mode; also by decreasing the bowing distance, the pressure required to maintain the motion is also to be increased.

The periodic force expressed by (27) plus an arbitrary constant must be equal to the pressure applied by the bow; if w represent the relative speed of the bowed point with respect to the bow during its descent, then we have the frictional force $Q=F_0+F$. Let F' be the maximum value of

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[12] Equations (27) and (28) are due to Prof. Raman.

F during the forward motion of the bowed point; then if Q$'$ is the maximum value of the frictional force

$$
\begin{aligned}
Q' &\nless F_0+F' \\
P\mu_s &\nless F_0+F' \\
\text{Hence } P\mu_s-Q &\nless F'-F \\
\text{and } Q &= P\mu_d \\
\therefore\ P &\nless \frac{F'-F}{\mu_s-\mu_d}
\end{aligned}
$$

where P = bowing pressure, μ_d, and μ_s are dynamic and static coefficients of friction. In the case of the fundamental vibration only

$$
\begin{aligned}
P &\nless \frac{F\text{max}-F\text{min.}}{\mu_s-\mu_d} \\
&\nless \frac{2\,F\text{ max}}{\mu_s-\mu_d} \qquad \ldots \qquad (29)
\end{aligned}
$$

F_{max} corresponds to the maximum value of F when the fundamental only is retained in (27). Below are given tables of the values of α and β and other necessary constants for determining the bowing pressure. The determination of the coefficient of friction in the actual case of resined bow and wire is a matter of considerable difficulty. The dynamical coefficient is a function of the relative speed w. Lippich[14] devised a method for the determination of the coefficient of friction in the case of plates of wood, leather, and resin. His method consisted in rubbing the experimental plate against a hard rubber imbedded along the edge of a revolving wheel. The experimental plate is kept pressed against the wheel by a suitable pressure just on the top of the wheel by applying equal and opposite tensions on the two sides regulated by means of weights in the manner of Rowland's arrangement for the determination of mechanical equivalent of heat; in the present case the axes of the revolving wheel is horizontal and the weights had the tendency to move the experimental plate in the horizontal plane. The frictional force is balanced by adding or subtracting weights. The frictional coefficient has been determined (1) under static conditions and (2) under dynamic conditions. Lippich has shown that in all cases he examined, the frictional force could be represented by the formula of the type

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[14] Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften Math.. Natur Klasse Band CXXIII, p. 1071 (1914). (Wien).

$$F=D\left[\frac{F_o-f}{1+aw}+f\right];$$

the terms in the bracket give the coefficient of friction when the relative speed is w, D is the pressure in gms. f and a are constants, and F_0 is the static coefficient. Now we have complete data for determining the bowing pressure.

For $l=63$, $\frac{x_o}{l}=\frac{1}{8}$ $r_1=1$, $k=8\cdot8\times10^{2}$, $a_1=2\cdot3$. $To=1\cdot7\times10^{6}$

$$a=\frac{1\cdot04\times10^{2}}{m(r^2-1)+7\cdot7\times10^5/m(r^2-1)}$$

TABLE (5)

Freq.	$m\times10^{-3}$	r^2-1	$m(r^2-1)\times10^{-3}$	a
200	1·25	2·61	3·26	$8\cdot0\times10^{-2}$
250	1·57	1·61	2·53	$8\cdot6\times10^{-2}$
300	1·88	·58	1·0	$6\cdot\ \times10^{-2}$
380	2·4	0	0	0
450	2·8	$-\cdot3$	$-8\cdot46$	$-5\cdot9\times10^{-2}$
500	3·1	$-\cdot36$	$-1\cdot14$	$-5\cdot7\times10^{-2}$
600	3·76	$-\cdot60$	$-2\cdot2$	$-4\cdot0\times10^{-2}$
700	4·4	$-\cdot75$	$-3\cdot1$	-3×10^{-2}

$$\beta=\frac{9{\cdot}15\times10^{4}}{[m(r^{2}-1)]^{2}+k_{1}^{2}}$$

TABLE (6)

Freq.	$\{m(r^{2}-1)\}^{2}$	β
200	$10{\cdot}6\times10^{6}$	$8{\cdot}1\times10^{-3}$
250	$6{\cdot}4\times10^{6}$	$1{\cdot}3\times10^{-2}$
300	$1{\cdot}21\times10^{6}$	$4{\cdot}6\times10^{-2}$
380	0	$1{\cdot}2\times10^{-1}$
450	$7{\cdot}1\times10^{5}$	$6{\cdot}2\times10^{-2}$
500	$1{\cdot}3\times10^{6}$	$8{\cdot}84\times10^{-2}$
600	$4{\cdot}8\times10^{6}$	$1{\cdot}6\times10^{-2}$
700	$9{\cdot}6\times10^{6}$	$8{\cdot}8\times10^{-3}$

TABLE (7)

Freq.	D_1	E_1	F_1 gms.
200	·06 cm.	$4{\cdot}86\times10^{-4}$	1·27
250	·05	$6{\cdot}5\times10^{-4}$	2·14
300	·03	$1{\cdot}37\times10^{-3}$	5·5
380	·025	3×10^{-3}	15·0
450	·020	$1{\cdot}24\times10^{-3}$	9·1
500	·020	$1{\cdot}76\times10^{-3}$	11·5 *
600	·020	$3{\cdot}2\times10^{-4}$	2·52
700	·020	$1{\cdot}76\times10^{-4}$	1·62

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* Two terms of the series have been included. $k_2=2\times10^{1}$, found experimentally by loosening the bearings.

The minimum bowing pressure is given by (29), μ_s-μ_d has been evaluated from Lippich's experimental values. Rigorously, his values are not applicable to the present case, but since the wire is covered with a coating of resin, the frictional coefficient will be approximately the same as that between a resin plate and hard rubber whose surface is expected to be covered with resin powder after a few revolutions of the wheel; his values will therefore be near the true ones.

$$F_0=1\cdot07$$
$$f=\cdot37$$
$$a=1\cdot4$$

and $w=2\cdot7$ meters calculated from §5, and μ_s-μ_d= ·5.

TABLE (8)

Freq.	200	250	300	380	450	500	600	700
Bowing pressure in gms.	5·1	8·6	22·0	60·0	36·4	44·0	10·1	6·5

A fair agreement is found between the calculated and observed values. It has also been shown that by taking two terms of the series, the values of the bowing are found to increase at the resonance pitches of the diaphragm and the horn. Beyond the resonance points, the bowing pressure is more or less constant; exact concordance between the calculated and observed values has not been obtained, this is no doubt due to the uncertainty in the value of $\mu_s-\mu_d$ and the omission of the cosine components.

§ 6

EMISSION OF SOUND FROM THE INSTRUMENT.

(a) *Experimental determination of sound emission.*

The emission of energy in absolute units from different instruments has been measured by Paul E. Sabine[15] and Prof Edwards.[16] Sabine's method consisted in the determination of the duration of sound in a hall whose acoustic properties are known. If E be the flux of energy per second from the source, it is given by

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[15] Phys. Rev. Vol. 22, p. 305 (1923).

[16] Phys. Rev. Vol. 32, p. 31 (1911).

$$\log_{1}.\mathrm{E} = vat_1/18\,\mathrm{V} + \log_{10} 2500\, a/\mathrm{J}$$

t_1 = duration of sound,
V = Volume of room,
a = absorbing power,
J = threshold intensity.

He found in the case of violin cello the emission per second to vary between 10^3 to 10 ergs at different frequencies. The method that was finally adopted is the following. It consisted in measuring the deflections of a Rayleigh disk suspended near the mouth of a resonator in unison with the source. The couple exerted by the air current is given by

$$\mathrm{M} = \frac{4}{3}\rho a^3 \mathrm{W}^2 \sin 2\,\theta.$$

a = radius of disk,
w = mean velocity of air,
ρ = density of air,
and θ = inclination of the disk to the plane of the moth.

The mean kinetic energy of the vibrating air near the mouth is given by

$$\frac{1}{2}\rho \mathrm{W}^2$$

and multiplying the above quantity by

$$\left(\frac{2\mathrm{R}n}{v}\right)^2,$$

where R = radius of the mouth, n = frequency, v = velocity of sound in the medium, we get the kinetic energy of the vibrating air at that place when the resonator is absent, and hence the energy per unit volume.

$$M=\mu\phi$$

where ϕ is the deflection of the disk μ=couple per unit twist. μ is found from an auxiliary experiment from the formula

$$u=\frac{4\pi^2 I_0}{T_2^2-T_1^2}$$

where I_0 is the known inertia of the additional system, T_1 and T_2 are periods of oscillation before and after addition of the inertia in the form of a piece of fine glass fibre. In the experimental method a silvered mica disk cut circular was suspended by a quartz fibre drawn very fine, about one meter long. To make the system stable a glass cylinder 3cm. long and 5 mm. diameter and provided with a small bead 1 mm. diameter, was fixed longitudinally to the lowest point of the disk. The bead was kept immersed in machine oil to damp vibrations. When W^2 is stationary, the deflection ϕ will be permanent, and damping will have no effect on the magnitude of deflections, on the other hand oscillations are quickly damped. In the experiments the disk was suspended at an angle of 45° to the plane of the mouth of the resonator, which was cylindrical and whose length could be varied by the telescopic arrangement. There were three such resonators which could control the full range of frequencies. The deflection was measured by the shift of a spot of light reflected from the mica mirror. The distance of the mica disk from the mouth was kept constant; and the whole was kept inside a glass case having an opening to allow sound waves to enter.

The violin was played at a distance of 8 meters from the mouth and deflections were noted when a steady tone with the least pressure of the bow was obtained. The resonators were brought in unison with the fundamental, and unisons were tested by auxiliary organ pipes of different frequencies. The deflections were now proportional to the energy of the fundamental. Table (6) gives the result of five sets of experiments.

Distance of scale from mirror

$$=38\text{cm. } \mu=4\cdot28\times10^{-3} \quad a=\cdot5\text{cm.; } \sin2\theta=1,$$

hence the average energy E per c. c. is given by

$$E/2=\frac{\rho\omega^2}{2}.\left(\frac{2Rn}{v}\right)^2=\frac{3\mu\phi}{8a^3}.\left(\frac{2Rn}{v}\right)^2$$

$2R=1\cdot5$ c. m. $v=340$ metres, $n=$frequency.

$$E/2=3\cdot28\times10^{-13}\ n^2d \text{ ergs per c. c.}$$

where $d=$deflection in cm.

TABLE (9).

Freq.	Deflection.	E/2 erg./cm^3
216	2·1 c. m.	$\cdot21\times10^{-6}$
340	5·0	$1\cdot9\times10^{-7}$
384	31·0	$1\cdot5\times10^{-6}$
400	30·0	$1\cdot57\times10^{-6}$
440	21·0	$1\cdot32\times10^{-6}$
465	21·0	$1\cdot49\times10^{-6}$
475	14·0	$1\cdot03\times10^{-6}$
510	18·0	$1\cdot53\times10^{-6}$
635	12·0	$1\cdot58\times10^{-6}$
662	12·0	$1\cdot80\times10^{-6}$

Since the experiments were performed in a room with closed doors, the energy density reached after a short time is related to the acoustic power of the source by the formula given by Prof. W. C. Sabine.

$$g/_2 \mp i_n \cdot 8{\cdot}6 \times 10^8 \times a$$

where a=absorption expressed in terms of square meters of open window. In the present case $a=17$, hence

$$g/_2 = 1{\cdot}46 \times 10^9 \times i_n$$

where E_n is given in the previous table.

TABLE 10.

Freq.	216	340	384	400	440	465	475	510	635	682
g/2 ergs per sec.	$4{\cdot}7 \times 10^1$	$2{\cdot}8 \times 10^3$	$2{\cdot}2 \times 10^3$	$2{\cdot}3 \times 10^3$	$1{\cdot}9 \times 10^3$	$2{\cdot}2 \times 10^3$	$1{\cdot}5 \times 10^3$	$2{\cdot}2 \times 10^3$	$2{\cdot}3 \times 10^3$	$2{\cdot}6 \times 10^3$

The above table shows that the radiation of energy increases considerably near the resonance of the diaphragm, and the horn. The flux at the resonance pitch is about 25 times as great as at the low frequencies, and 3/2 times the energy flux at high frequencies. The maximum at horn resonance is due to the fact that the pressure variation within the horn at the horn resonance, is smaller than at other frequencies, and therefore greater amount of work is done to produce motion of air. In fact the pressure at any point within the horn is the sum of two parts, p_1 and $-p_2$ which differ in phase by $\frac{\pi}{2}$, hence the pressure within the pipe is greatest when p_2 is least. This happens when resonance takes place and then the work done in the forward direction pV is greatest. A calculation will presently be given for the radiation of energy from the conical horn at different frequencies of excitation.

(*b*) *Theory af the conical horn as radiator of sound.*

The theory of horns of various profiles has been given by the late Prof. A. G. Webster,[17] when used as receivers. His experiments with horns provided with a hollow cylindrical attachment to the cone, show that when the length of the cylinder is large and comparable to the wave length in the horn, there is harmonic variation of pressure within the cylinder, while when its length is short, the pressure is constant over the extreme free end, and then it begins to fall. Prof. Stewart's[18] theory of the optimum angle of horns used as receivers, will be followed in the present investigation. For reasons mentioned above when the length is short, we can ignore the presence of the cylindrical attachment and consider the cone to begin from $r=r_0$ where r_0=radius of the cylinder. Let ϕ represent the velocity potential inside the horn, and ψ the same outside, and r=radial distance and

$$k=2\pi/\lambda$$

$$r\phi=(A\sin kr+B\cos kr)\,e^{int} \tag{30}$$

$$r'\psi=Pe^{-ikr'}\,e^{int} \tag{31}$$

The maximum pressure at the vertex of the cone when $r=r_0$

$$p_{\max}=\rho nkA\left(1+\frac{a}{r_0k}\right) \quad \cdots \tag{32}$$

$a=B/A$, ρ density of air.

The current across a hemispherical surface of radius r'

$$=2\pi(r')^2\frac{d\psi}{dr}=-2\pi P$$

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[17] Proc. National Academy of Sciences, Vol. 5, p. 275 (1919) also Vol. 6, p. 316 (1920).

[18] Phys. Review, Vol. 25, p. 280, p. 225 (1925).

This must be the same as the current across the open end of the cone, hence, approximately,

$$\frac{\sigma k \mathrm{A}}{l}\left[\{\cos kl-\sin kl\}-\left\{\frac{\sin kl}{lk}+\frac{a\cos kl}{lk}\right\}\right]=-2\pi \mathrm{P} \tag{33}$$

Again the current must be equal to the conductivity of the open end multiplied by the difference in the velocity potentials.

$$\frac{\sigma}{c}\,\frac{k}{l}(\mathrm{A}\cos kl-\mathrm{B}\sin kl)=\psi_0 r'-\phi_i \text{ approximately} \tag{34}$$

σ = area of open end.

c = conductivity.

r'_0 = radius of the open end.

l = slant length of the cone.

We get from (32), (33) and (34)

$$(1-a\tan kl)+(a+\tan kl)=\frac{c}{r'_0}(1-a\tan kl)$$

Putting $\sigma_1=\dfrac{c}{r'_0}$

We get

$$\tan kl=\frac{\sigma_1-(1+a)}{\sigma_1 a+(1-a)} \qquad \ldots \tag{35}$$

The value of c will lie between 0·6 and unit times the radius of the month; since the opening is large, we assume $c=r'_0$, and then

$$\tan kl=-a \tag{36}$$

It is not difficult to work out the results for any smaller value of the conductivity.

TABLE (11)

$l=33$; $r_0=1$; $r'_0=6$ cm.

$2\pi/k$	100	90	80	70	65	60	55	50	45	40
a	1·4	·84	·41	0	−·25	−·58	−1·×2	−3·08	+5·67	+1·0

When a is known, A, B, and P are determined in terms of the maximum pressure at the vertex. We find that $a=0$, when $kl = m\pi$, *i.e.*, at the resonance frequencies. For smaller wave lengths, the formulæ do not hold good, but the general result is clear.

When the wave length is greater than twice the length of the pipe, the pressure falls regularly from the vertex; while when it is smaller than twice the slant length, calculation shows that pressure falls rapidly as we move away from the vertex, becomes zero, and assumes negative values as we cross the zero point. Curves were drawn (not reproduced) and they were found to agree with the pressure curves given by Prof. Webster. At the resonance frequencies the pressure variation within the horn is given by

$$p = p_m \sin kr/kr. \quad \dots \quad (36a)$$

which agrees with that given by Prof. Webster. Of course (36*a*) holds good from $r = r_0$ to $r = l$. At other frequencies a is finite and the cosine factor is always negative, hence the pressure gradient is always greater than (36a).

Energy radiated from the horn.

For a given value of the maximum pressure at the vertex, the radiation is given by[19]

$$E_0 = \frac{k^2 \rho v}{8\pi} \sigma P^2 \text{ over a sphere.}$$

Putting the value of P we get

$$E_0 = \frac{p_m^2 (r'_0)^6}{\rho v l^2 32} \left(\frac{\sec kl}{(1 + a/k)} \right)^2$$

$$= 3\cdot0 \times 10^{-2} p_m^2 f^2$$

$$r_0 = 1, \text{ when } kl = m\pi, f = 1.$$

Hence maximum energy is radiated outwards when $kl = m\pi$.

TABLE (12).

λ	100	90	80	70	60	50	40	85
f^2	·005	·01	·03	1·0	·063	·02	·05	1·0

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[9] Lamb's Dynamical Theory of Sound § 76, p. 229 (new edition).

The above table shows how radiation varies for different wave lengths. At high frequencies the values of f^2 are not accurate, but the general tendency is shown clearly. The resonance is very sharp, and the radiation reaches a limiting value on either side of the resonance pitches.

(*c*) *Calculation of* p_m.

The maximum pressure generated at the vertex can be calculated from the dimensions of the air chamber enclosed by the diaphragm and the end of the cylindrical attachment. Since the pressure is constant over a small part of the cylinder, and the inertia of the air in the cylinder and the horn is large, the extreme end will behave like a closed end [see Fig. 3], and then the calculation of p_m means the evaluation of the volume of air pushed in by the diaphragm. The conditions are otherwise when the horn and the cylindrical attachment are removed. Two cases of interest are given here.

(1) When the diaphragm is clamped at the edge, and there is no horn or cylinder.

(2) When the diaphragm moves to and fro as a rigid body in an opening provided with infinite flange.

Case (I). Lamb has given a calculation for the velocity potential of the medium in the neighbourhood of the plate

$$\phi=\frac{\pi^{\frac{1}{2}}\Pi(\frac{1}{2})}{2.\Pi(5/2)}\mathrm{F}\left(-\tfrac{5}{2},\tfrac{1}{2},1,\frac{r^2}{a^2}\right)a\frac{dc}{dt}$$

for a prescribed motion

$$y=c\left(1-\frac{r^2}{a^2}\right)^2$$

where r=radial distance from the centre of the plate. At $r=0$, the maximum value of

$$\phi=\frac{\pi^{\frac{1}{2}}\Pi(2)}{2\Pi(5/2)}a\frac{dc}{dt}$$

The pressure p'_m is then given by

$$p_m' = \frac{8}{15} a p^2 \rho A \qquad \ldots \quad (36c)$$

$p/2\pi$=frequency, a=radius of diaphragm,

A=amplitude of vibration of the same.

Case (II). Lord Rayleigh's formula[20] shows that p_m'' in this case is given by

$$p_m'' = \frac{\rho p^3 a^2}{2v} A \qquad (37)$$

Case (III). When the horn is attached and the enclosed chamber behaves like a closed one, the pressure developed by the displacement of the diaphragm can be calculated as follows. If we assume that the diaphragm moves in such a way that the shape at any instant is a part of a sphere, then the volume of air displaced will be

$$\tfrac{1}{3}\pi r^2 A$$

the actual volume will be less.

$$p_m = v^2 \rho \frac{dv}{V} = \rho v^2 \tfrac{1}{3} \frac{\pi r^2 A}{\pi r^2 b} \qquad \ldots \quad (38)$$

At the resonance of the diaphragm

$$A = \cdot 456 \times 10^{-3} \ cm.$$

determined from photographic record and $b = \cdot 55$ cm. the thickness of the disk of air between the diaphragm and the end of the cylinder.

$p_m' = 1 \cdot 94 \times 10^{-3}$ dynes per sq. cm.
$p_m'' = 6 \cdot 83$ „ „ „
$p_m''' = 4 \cdot 15 \times 10^{2}$ dyn sq. cm.
$p/2\pi = 380$.

---

[20] Theory of Sound, Vol. II, p. 165 eq. (12).

Hence we see that the effect of the flange and the horn is to increase the pressure that is developed near the diaphragm for a given displacement. This explains why little sound is produced when the horn is removed, or there is no flange near a vibrating diaphragm.

(*d*) *Evaluation of absolute energy.*

Corresponding to the three cases the radiation is given by

$$R' = \frac{\pi p^4 \rho a^4}{36v} A^2 \quad \dots \quad (39)$$

$$R'' = \pi p^4 \rho \quad \dots \quad (40)$$

$$R''' = 3 \cdot 10^{-2} p_m{}^2 f^2$$

Putting the values of A and p_m, etc.

$R' = 7 \cdot 4 \times 10'$ ergs per sec.

$R'' = 6 \cdot 7 \times 10^2$ " " "

R''' = Stroviols radiation

$= 5 \cdot 16 \times 10^3 \quad f^2 = \cdot 01.$

The radiation in the above case can be evaluated by the formula

$$R''' = f^2 pm \frac{dv}{2} 2n. \text{ per sec.}$$

dv = volume pushed in

n = frequency.

$= 6 \times 10^3$ ergs per sec.

The two calculations lead to the same value of radiation. We thus find that the presence of the flange increases radiation about ten times, while the presence of the horn and the cylindrical attachment increases radiation hundred times, hence the utility of a small flange, and horns in all round radiators is explained. The author hopes to make exact calculation of the case where there is a small flange—a case very greatly used in practice.

The calculated value of radiation at the resonance pitch of the diaphragm is $5{\cdot}1 \times 10^3$ ergs per second while the experimentally determined value is $4{\cdot}4 \times 10^3$ ergs per second. The slight discrepancy is not surprising considering the roughness of the experimental methods used.

§ 7

SUMMARY AND CONCLUSION

(1) A verification of the theory of bowed instruments, has been made by using the Stroh violin which consists of simple mechanical systems. It shows an abnormal increase of the radiation of the order $4{\cdot}4 \times 10^3$ ergs per second at the resonance pitch of the diaphragm while at low frequencies it falls down to $9{\cdot}4 \times 10^1$ ergs per second, and at high frequencies the radiation amounts to $5{\cdot}2 \times 10^3$ ergs per second. There is also a rise at the resonance pitch of the horn.

(2) The damping co-efficient of the string has been determined at different frequencies. There is considerable rise in the damping co-efficient of the order 3×10^2 at the resonance pitch of the diaphragm, at other frequencies it is of the order 10. Theoretical calculations of the damping co-efficient from the constitution of the instrument show a fair agreement with the observed values.

(3) The minimum bowing pressures have been determined at different frequencies. Bowing pressure is of the order of 7 gms. except at the resonance pitch of the diaphragm where the bowing pressure rises to about 50 gms. A calculation of the bowing pressures shows a fair agreement with the observed values. Incidentally the theory of forced vibration of the string under an impressed force of the type ($E_1 \cos mt + E_2 \sin mt$) has been given. This theory takes into consideration the coupled vibration of the bridge and determines the bowing pressure.

(4) A simple theory of conical horns as radiators of sound has been given. It has been found that the emission of sound is maximum at the resonance pitch of the horn. The emission has a sharp peak when graphed against pitch, while at other frequencies radiation has a limiting value.

(5) From the motion of the diaphragm the pressures that are developed are calculated, and finally the radiation is evaluated in terms of the pressure generated. The radiation at the resonance pitch of the diaphragm comes out to be $5{\cdot}1 \times 10^3$ ergs per second, while the experimentally determined value is $4{\cdot}4 \times 10^3$ ergs per second. With these calculations it has been shown that the attachment of a flange, or horn increases the output considerably.

The author begs to record his deep thanks to Prof. C. V. Raman, F.R.S., at whose suggestion this work was undertaken for placing the facilities of the laboratory of the Indian Association for the Cultivation of Science at the disposal of the writer.

ALLAHABAD:
1st July, 1926.

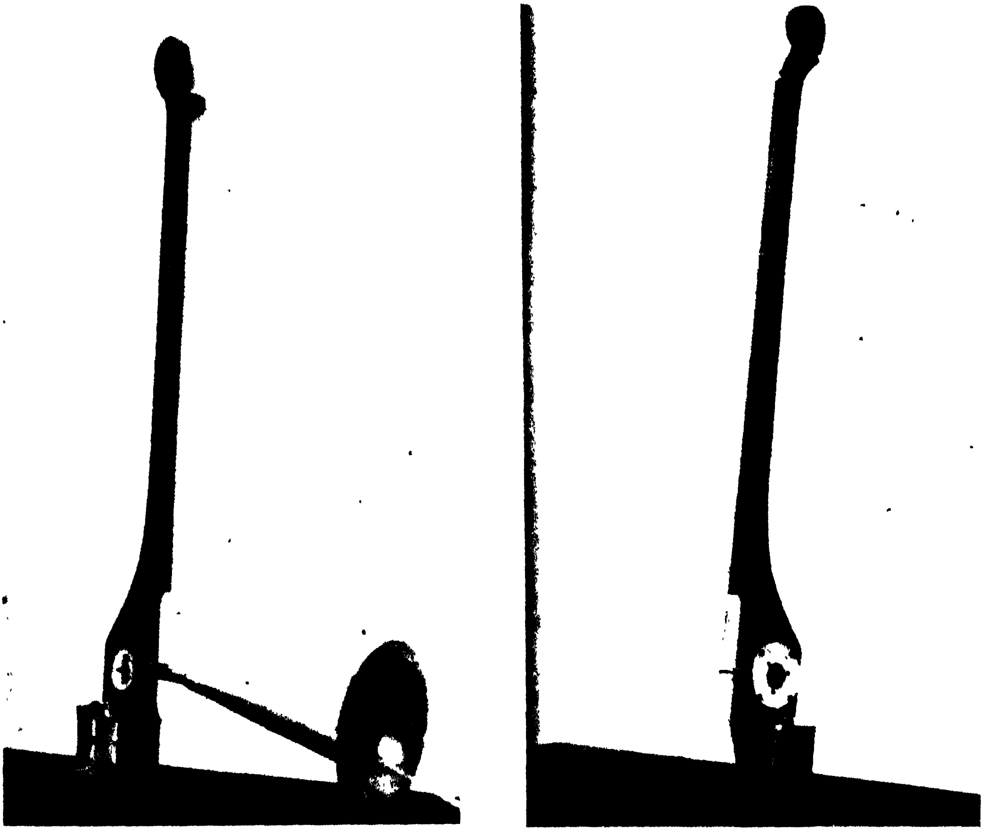

Fig. 1

Picture of Stroh Violin

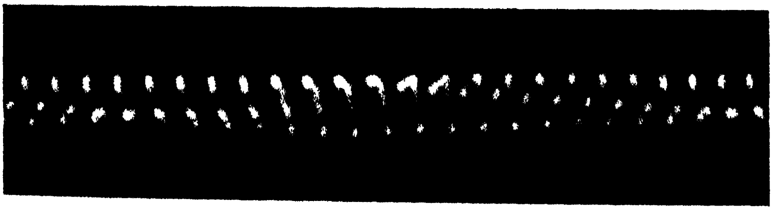

Fig. 5

Wolf Note

9. On the Magnetic Susceptibilities of Gases at Low Pressures.

BY

V. I. VAIDYANATHAN, M.A.,

Research Scholar in the Indian Association for the Cultivation of Science.

1. INTRODUCTION.

From the standpoint of the molecular theory of magnetism the study of the magnetic behaviour of gases at low pressures is of considerable interest. Due to the great experimental difficulties nothing seems to have been done in this direction till 1924, when A. Glaser[1] published results of a series of investigations on the diamagnetic susceptibilities of carbon-dioxide, nitrogen, etc. He noticed that the volume susceptibitities remain proportional to pressure up to a certain point, but deviate from proportionality at lower pressures, being greater than the theoretical value in the ratio 1 : 3. His method consisted in measuring the changes in the rotatory couple on a paramagnetic glass rod, suspended at its centre of gravity and placed between the pole-pieces, when surrounded by the gas at different pressures. To make the method a practicable one, extremely elaborate arrangements were necessary to secure constancy of the temperature of the glass rod and of the magnetic field.

A well-known method of measuring susceptibility is to determine the translatory force on the test specimen, when placed in an inhomogeneous field. It was thought interesting to investigate the problem by the latter method, but the arrangements usually adopted are not sufficiently sensitive for such an investigation with gases.

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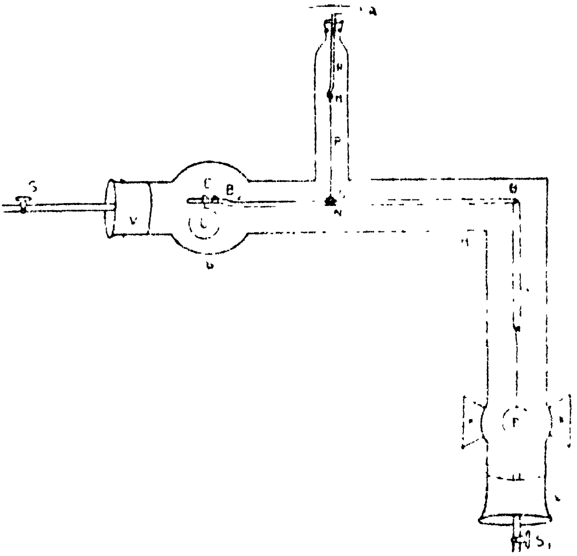
[1] A. Glaser, Ann. der Physik, 75, 459 1924. 78, 641; 1925.

Towards the beginning of this year the author succeeded in evolving a very sensitive apparatus by which the method could be used for the investigation of the susceptibility of gases at low pressures.

2. THE SUSCEPTIBILITY BALANCE.

FIG 1



B_1 B_2 is a thin aluminium vane 17 cms. long. The longer arm OB_1 is about 11 cms. It is suspended by a phosphor-bronze strip P about 8 cms. in length (No. 8253, Messrs. Pye & Co.). N is a concave mirror for the lamp and scale arrangement, and serves to read the deflection of the beam. The suspension at H_1 is made by first getting the beam into the required position and trapping the fine hook at H_1 in the V groove of the rod R. The hook fits into the groove and is attached to it with shellac. The rod R passing through an air-tight head can then be tightened up, bringing the beam centrally. L is a silk loop to which the bulb B is attached by a hook. C is a counterpoise bulb whose volume is adjusted in relation to that of B, so that the hydrostatic effect of introducing the gas into the apparatus is exactly compensated. C_1 is an additional counterpoise for securing the equilibrium of the beam. V, V_1, are rubber-corks fitting the two ends of the air-tight balance chamber G H K. At G the chamber is blown out to a bulb and at K it is widened in a plane at right angles to that of the figure. The bulb at K is slightly conical and approaches the narrow gap between the pole-pieces. The total weight of the suspended system does not exceed 4½ grams. The range of movement of B corresponds to about 200 divisions of the spot of light on a scale placed at a distance of 100 cms.

The new features of the apparatus are, that the balance itself is suspended in an atmosphere of the gas under investigation and is enclosed in the balance chamber G H K, and that the closed bulb B, suspended in the magnetic field, is rendered magnetically neutral. The chief difficulty in most of the previous torsion methods was that the glass bulb used for enclosing the gas, or the rod suspended in an atmosphere of the gas (for instance Tanzler's[1] and Glaser's[2] experiments) had enormous susceptibility and mass, and the force on the gas itself, in the magnetic field, is comparatively very small. The magnetic properties of CO_2, N_2, H_2, etc. are so feeble that an accurate investigation is extremely difficult under such conditions. The author got out of this difficulty as follows and this being done, it was possible to use fine phosphor-bronze strips for the the suspension of the balance beam.

Various specimens of glass were magnetically tested and one having a very low diamagnetic susceptibility is blown out into a thin uniform bulb, with a narrow stem. The actual bulb used had a diameter of 17·5 mms. and a weight of 0·45 grams. The pressure of air in the bulb was adjusted by temperature control, to compensate for the diamagnetism of the glass, and the thin stem was fused. To test if the compensation has been effected, it is suspended to the loop L and the field put on, after evacuating the chamber G H K. From the direction of deflection of the spot of light, whether the compensation is effected or not can be known. By systematically repeating the above processes, nearly complete compensation can be effected. Exact compensation for zero susceptibility is not so easy with such an arrangement. Even if it is effected at one temperature, it is disturbed under other conditions due to the paramagnetic air changing its susceptibility according to Curie's law. Nor is any such ideal adjustment necessary for our purpose. All that we require is a system possessing a susceptibility of the order of feebly magnetic gases and hence controllable by the torsion of a phosphor-bronze strip.

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[1] P. Tanzler, Ann. der Physik, 24, 931; 1907.

[2] A. Glaser. *Loc. cit.*

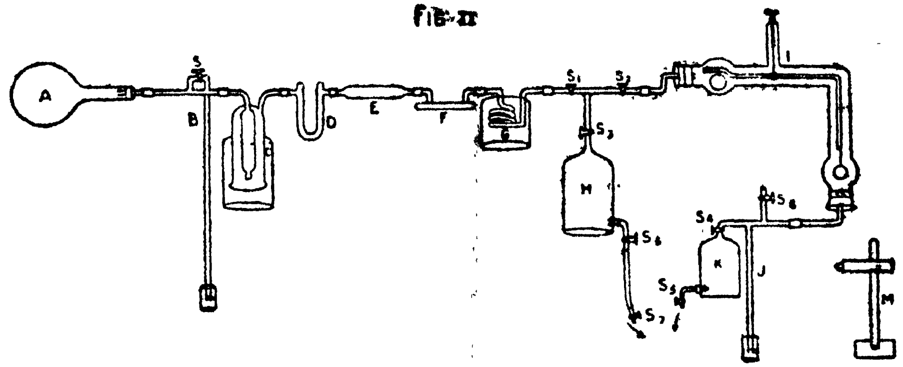
The apparatus is found to be very sensitive in practice. Arrangements for the introduction of gas and regulation of pressure were such as not to disturb the apparatus mechanically. The connecting glass tubes etc. are made as long as is consistent with convenience. This ensures that any change in deflection is due to the change of the susceptibility of the surrounding medium only.

The method of measurement is based on the magnetic analogy to the principle of Archimedes which Faraday found to hold true in gases. The susceptibility of the suspended system remaining constant, the change in deflection is proportional to the change in the volume susceptibility of the surrounding medium.

3. EXPERIMENTAL ARRANGEMENTS.

The complete experimental arrangements for preparation, purification and investigation of carbon-dioxide are shown diagramatically in Fig. II.

Fig. II



The pyrex flask A contains sodium bicarbonate (Merck's reagent). B is a manometer and serves as a safety valve. C is an empty tower kept cooled in ice, to condense the water escaping during the preparation of the gas. D is a calcium chloride U tube, fused in order to make it completely air-tight. E is a hard glass tube containing freshly reduced copper gauze. F is a second calcium chloride tube and G a long spiral. The spiral is kept immersed in ice in order to cool the gas before finally collecting it in the holder H. This enables the filling of the gas at about atmospheric temperature. Subsequent fluctuations of temperature do not reduce it very much. Thus without further arrangements, there is sufficient gas for investigations up to about one atmosphere. The volume of the gas holder was about 5 litres and of the balance chamber about half a litre. J is a second manometer fitted with a scale, reading to a millimetre and K an aspirator connected to the balance chamber and a Cenco-Hyvac pump and M a cathetometer. S_1,S_2 etc., are stop-cocks.

Pure carbon-dioxide is prepared by heating sodium bicarbonate contained in A. The apparatus from A to H is completely evacuated before finally filling H with the gas. During these operations the stop-cock S_2 remains closed. The gas is passed through H for 2 hours and that escaping at S_7 is analysed. The caustic potash solution absorbed the gas completely and the heated gauze showed no trace of oxidation. The stop cocks S_1, S_3, S_6, S_7 are closed and the gas left over-night to attain atmospheric temperature.

4. METHOD OF EXPERIMENT.

Before investigating the gas, K is connected to the pump and the balance chamber is completely evacuated. The rotatable head of the balance is turned so that the bulbs stand centrally with sufficient freedom of movement, when the field is on. A small quantity of air, sufficient to increase the pressure by about a millimetre, is now let into the balance chamber and the change of deflection observed. The cathetometer serves to read the pressure accurately. The pressure is carefully increased and the respective deflections with air in the magnetic field are observed up to a pressure of 8 to 10 mms. This process is intended to calibrate the scale, for obtaining the relative susceptibility of carbon-dioxide with respect to air.

The balance chamber is evacuated again, flushed many times with carbon-dioxide and exhausted repeatedly. The gas in then slowly admitted by partially opening S_3 and S_2, till the pressure increases to about 8 or 9 cms. On introducing the field, the balance is deflected and oscillates about a mean position. When the oscillations are sufficiently damped to about 2 or 4 divisions of the mean position, the deflections are observed. Readings when the pressure of carbon-dioxide diminishes are taken after an interval of 4 hours to allow for temperature equilibrium. The shifts in the zero reading between different series of investigations are due to the temperature fluctuations and do not affect the results.

5. Results.

TABLE :—I

Mean temperature—31·4°C.

Carbon-dioxide.

Readings of the spot of light.	P in mms. of mercury.	Relative deflections
223·4	0	0
231·3	92	7·9
246·0	156	20·6
254·2	240	30·8
266·2	316	42·8
279·2	396	55·8
288·0	484	64·6
294·0	568	70·6
306·9	650	83·5

TABLE :—II

Temperature—29·9°C.

Carbon-dioxide.

Readings of the spot of light.	P in mms. of mercury.	Relative deflections.
318	546	77·1
306·8	462	65·9
295·7	386	54·8
283·2	286	42·3
272·0	200	31·1
260·2	116	19·3
250·8	46	9·9
240·9	0	0

CARBON-DIOXIDE

FIG III

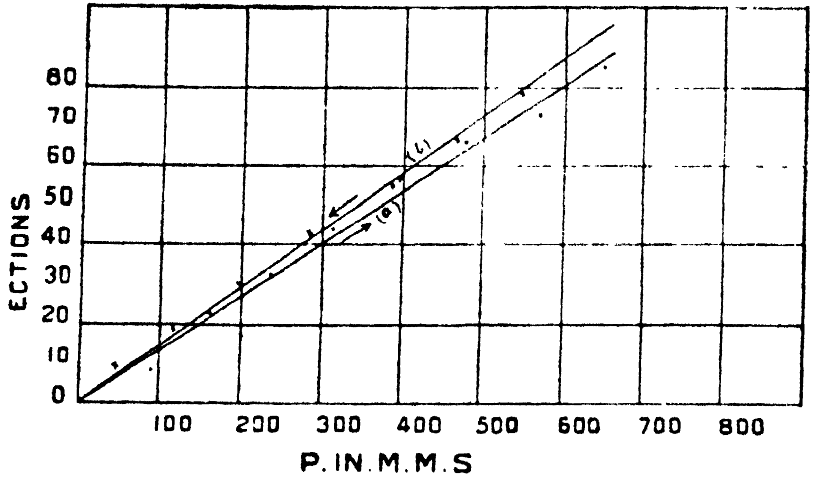


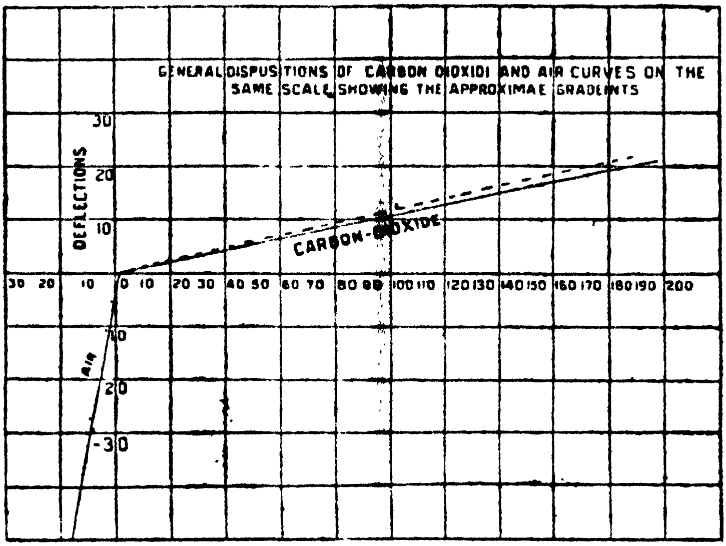
TABLE :—III

Relative deflections of air and carbon-dioxide. Mean temperature—30·5°.

Air		Carbon-dioxide		Air	
P in mms.	Deflection	P in mms.	Deflection	P in mms.	Deflection.
0	0	0	0	0	0
2·2	6·5	40	5	2·8	9
7	17·5	101	13	5·6	17
10·4	25·4	179	19		

The results of Tables I and II are shown in fig. III and of Table III in fig. IV, in which the readings obtained with air and carbon-dioxide are exhibited on the same scale. They show the approximate relative gradients.

FIG IV



The relative values (without correction for temperature) are obtained from figures such as IV. The mean of a number of such observations and calibrations gave after temperature correction, a relative value,

$$\frac{K_{CO_2}}{K_{air}} = -0{\cdot}0334$$

Taking Také Soné's[1] value; $0{\cdot}0308\text{x}10^{-6}$ for air at 0°C and 760 mms. pressure; this reduces to—$0{\cdot}00092 \text{ x } 10^{-6}$ for carbon-dioxide at 30·5°C and 760 mms. pressure.

6. Oxygen.

The arrangement described above is far too sensitive for use with a strongly paramagnetic gas like oxygen. Accordingly the apparatus used is a modified form of the manometric balance employed by Hector and Wills[2] in their determinations of susceptibility of oxygen, helium, etc., at high pressures. This modification rendered the arrangement more sensitive and enabled the investigation to be carried down to fairly low pressures.

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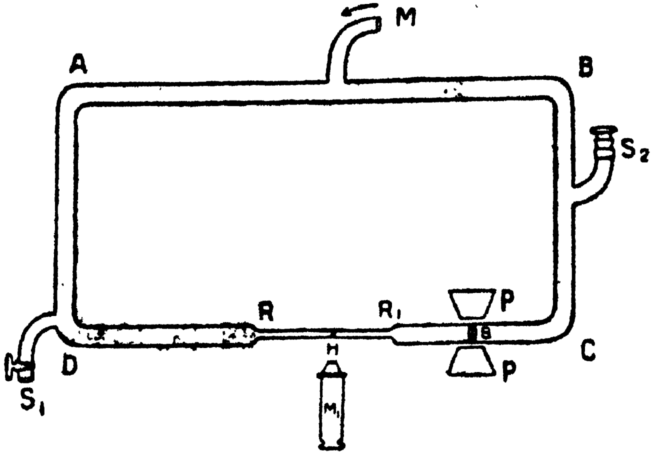
[1] Také Sone:—Phil. Mag., 39, 305; 1920.

[2] Hector and Wills. Phys. Rev. 23, 209; 1923. 24,418; 1924.

FIG V



This is shown in fig. V. ABCD is a rectangular glass tube, M the inlet for oxygen, S_1 a stop-cock and S_2 an air-tight plug. The internal diameter of the tube is about 6 mms. R R_1 is a small tubing joined to the wider one and has a diameter of about 2 mms. P. P. are the pole pieces H G is a column of solution. M_1 a microscope for observing the meniscus at H. At M the balance is connected to an elaborate arrangement for sending in oxygen and adjusting the pressure without the least disturbance to the balance. At G the solution and the gas are subjected to a strong magnetic field. When the solution of the liquid column magnetically balances against the gas, the volume susceptibilities of the gas and water vapour on the one side and the solution on the other are equal. The susceptibility of the solution can be deduced as follows:—

By the law of Wiedemann

$$m_l\lambda_l = m_w\lambda_w + m_s\lambda_s.$$

where m is the mass and λ the specific susceptibility. l, w, s, refer to the solution, water and salt dissolved respectively.

Let R denote the ratio $\dfrac{m_w}{m_s}$

Now $$m_l = m_w + m_s$$

$$\therefore \quad \lambda_l = \frac{R\lambda_w + \lambda_s}{1+R}$$

If $R = R_0$ when $\lambda_l = O$ then $\frac{R-R_0}{1+R}\lambda_w = \lambda_l$

If k_l denote the volume susceptibility then $k_l = \rho_l x_l$ (ρ denotes density).

$$\therefore \quad k_l = \frac{R-R_l}{[illegible]}$$

$\lambda_w = -0 \cdot 72 \times 10^{-6}$ according to Wills[3]

The other quantities are determined as follows. R is known by the careful analysis of a portion of a large volume of nickel chloride solution, prepared in boiled, distilled water and roughly adjusted to equilibrium at about 800 mms. and the room temperature. ρ_l is also measured under the same conditions of temperature. If to a known weight of this solution a definite volume or weight of water is added the new value, R_1 of R can be calculated. This solution (provided only a small quantity of water is added) balances against a lower pressure of oxygen. Obtaining a few readings and plotting the respective values of R, R_0 at the temperature of the experiment can be known. The respective ρ_l's also can be calculated assuming no change of volume. The chief determining factor is $R - R_0$ and depends on the chemical analysis and the accuracy with which the weight of water added can be known.

The method of experimenting is described below. A fairly large volume of the solution of nickel chloride is transferred to a clean dry flask. A small quantity of the solution is then introduced into the meniscus balance, through S_2, and

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[2] Hector and Wills (*Loc. cit.*).

[3] Wills. A. P. Phys. Rev. 20, 188; 1905.

moved along to wet it with the solution of required concentration. This is then got out at S_1. A second quantity just sufficient for occupying the length G H is let in again and the gas passed for a long time. The liquid column is moved along to ensure that air is displaced. S_1 S_2 are closed. ABCD is made perfectly horizontal and the solution got into the position G H. The field is put on and the pressure adjusted till the meniscus observed through the microscope, does not move on the removal or introduction of the magnetic field. The pressure, temperature, R and ρ_l are noted.

For a lower pressure:—A weighed amount of the solution (about 80 grams) is taken and water (about 1½ to 2 grams), from a carefully calibrated pipette is added. This solution is used for a second observation. ρ_l is calculated from the known density of water at the temperature of the room. The experiments were carried out in a double walled and fairly thermostatic room of the laboratory.

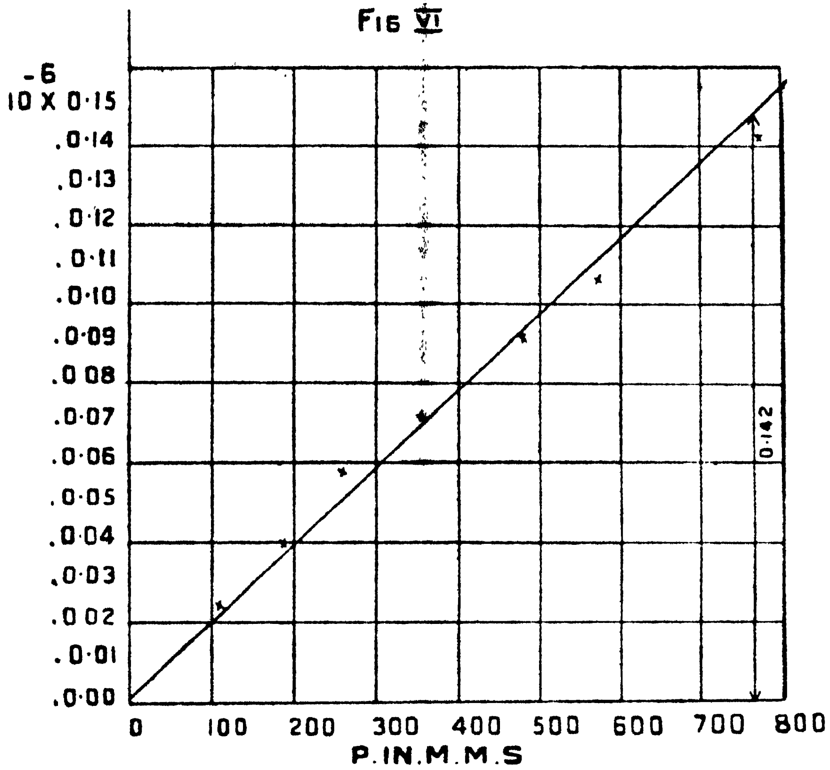
TABLE :—IV.

$R_0 = 49{\cdot}95$ Mean Temperature = 28·2°C Vapour pressure = 28·3mms.

Pressure of Oxygen in mms.	ρ_l	R	$K_{O_2} \times 10^{-6}$
778	$1{\cdot}027_8$	41·71	0·143
573	$1{\cdot}026_3$	43·45	0·106
482	$1{\cdot}025_6$	44·35	0·092
359	$1{\cdot}025_1$	45·37	0·072
260	$1{\cdot}024_8$	46·30	0·059
188	$1{\cdot}024_0$	47·23	0·041
84	$1{\cdot}023_8$	48·36	0·025

OXYGEN

FIG VI



Results of Table IV are shown graphically in fig. VI. R_0 is obtained by plotting the values of R and P of Table IV and producing the curve.

The volume susceptibility of oxygen as obtained from fig. VI $= 0\cdot142 \times 10^{-6}$ at 28·2°C and 760 mms. pressure.

7. Air.

The same method was used for air, yielding a value $0\cdot029 \times 10^{-6}$ at 27°C and 760 mms. pressure. The method was not found sufficiently sensitive for air at low pressures and a change of pressure of 1 to 2 cms. from the equilibrium position did not appreciably disturb the magnetic balance. Yet within the experimental accuracy the susceptibility k_{air}

was proportional to pressure. The approximate value obtained is intended as a check on other values.

8. REMARKS ON THE RESULTS AND THE METHODS.

In the torsion method the bifurcation of the two curves in fig. III is due to the temperature of the air, in the bulb B, rising during the experiment. The rise is indeed small, for the current in the magnet is run only during the instant of observation, and there is an asbestos pad, the wall of the balance chamber and the wall of the bulb to protect the air inside. The experiment is conducted in a double walled room of the laboratory and but for the heating of the magnet, it is thermostatic. A single series of observations does not require more than 30 to 40 minutes and the maximum rise in the neighbourhood of the magnet seldom exceeds ½ a degree. Still there is some effect. In curve (*b*) fig. III this error adds to the deflections when the pressure of CO_2 is reduced, being in the same direction. In (*a*) fig. III the deflection due to the rise of temperature tends to diminish that due to the increase of pressure of CO_2. The curve corresponding to the bisector of these two, is the ideal one which would be obtained after correction. In computing the relative value of $\frac{K_{CO_2}}{K_{air}}$ this is taken into account.

Since the torsion head was not rotated to bring the spot of light back into the original position, the bulb B moves in a small range of the field. In this range the product of the field and the field gradient is assumed to be constant. This was experimentally tested with deflections obtained in air and found constant within experimental errors. Over longer ranges there were small deviations, and the best position was selected for any series of observations.

The general result of the investigation is thus to indicate that within the limits of experimental error, the volume susceptibility of carbon-dioxide, measured by the translatory

tory movement of the gas in a direction at right angles to an inhomogeneous field, is proportional to pressure between ranges 0 and 700 mms. When this work was in progress a note on the same subject by Erwin Lehrer[1] appeared in Zeit. für Physik. Using the principle that the specific susceptibility of a diamagnetic gas is independent of temperature, he finds that the volume susceptibilities of carbon-dioxide and argon are proportional to pressure between ranges 60 and 720 mms.

In the method employed for the investigation of oxygen the susceptibility of vapour and its fluctuations are neglected. Oxygen being a strongly magnetic gas, this does not introduce any error beyond that of the experiment, even at low pressures. Small bubbles of air that still remained in solution, were evolved when the pressure was reduced. These were driven to the side H (Fig. V) beyond the magnetic field.

The volume susceptibility of oxygen was found to be proportional to pressure between ranges 100 and 800 mms.

9. SUMMARY AND CONCLUSION.

The diamagnetic susceptibility of carbon-dioxide was investigated by a new method; the volume susceptibility is found proportional to pressure between ranges 0 and 700 mms. The relative value $\frac{k_{o_2}}{k_{air}} = -0{\cdot}0834 \therefore k_{co_2} = -0{\cdot}00092 \times 10^{-6}$.

(Taking Také Soné's value $k_{air} = 0{\cdot}0308 \times 10^{-6}$)

The paramagnetic susceptibilities of oxygen and of air were investigated by counterpoising them against a solution of known susceptibility. The volume susceptibilities were found proportional to pressure, within the limits of experimental error. The values obtained were

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[1] Erwin Lehrer, Zeit, fur Physik ; 37, May, [illegible]

$$k_{O_2} = 0{\cdot}142 \times 10^{-6}$$

$$k_{air} = 0{\cdot}029 \times 10^{-6}$$

The work is still continued and further investigations by the torsion method and other details as field strength, *etc.*, will be published in due course.

The present work was carried out in the laboratory of the Indian Association for the Cultivation of Science, Calcutta. My best thanks are due to Prof. C. V. Raman, F.R.S., who suggested the problem, placed at my disposal the necessary apparatus, and helped me with kind suggestions during its progress.

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
210, BOW BAZAR STREET, CALCUTTA.
The 18th August, 1926.

The Scattering of Light by Liquid Surfaces.

BY

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(*MSS. Received for publication, 1st August, 1926.*)

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1. HISTORICAL INTRODUCTION.
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5. SURFACE PHENOMENA IN THE NEIGHBOURHOOD OF THE CRITICAL STATE.
6. SUMMARY AND CONCLUSION.

1. HISTORICAL INTRODUCTION.

The study of the phenomena forming the subject of this thesis had its origin in a suggestion due originally to Smoluchowski,[1] who, in his paper of 1908, on the thermodynamics of the critical state, pointed out that, as the surface of a liquid near the critical temperature has a very small tension, it should be subject to a large thermal agitation and hence exhibit an observable surface—opalescence in addition to the familiar critical opalescence, which is a volume-effect. Nothing seems to have been done to follow up this suggestion

[1] Smoluchowski, 'Annalen der Physik.' Vol. 25, p. 228 (1908).

till 1913, when Mandelstam[2] published some observations on the special case of the light incident on the boundary between the two layers of a mixture of carbon—disulphide and methyl alcohol near the critical solution temperature, at which the liquid develops a milky opalescence. Mandelstam noticed that, in directions very near that of regular reflection from the interface, there was also some scattered light, and conjectured from his somewhat meagre and qualitative observations, that the effect was analogous to that predicted by Smoluchowski for the critical state of a single liquid. Early in 1923, the present author, at the suggestion of Prof. C. V. Raman, took up the general problem of the light-scattering from optical boundaries and succeeded in observing the bluish white opalescence of the clean surfaces of transparent and metallic liquids at ordinary temperatures. Most of the outstanding features of the phenomenon, regarding the distribution of the intensity and the special polarisation effects for various angles of observation, were discovered about that time and a preliminary communication published in 'Nature,' August 25, 1923. The subject was then extensively developed, no fewer than sixty liquids being studied, and quantitative observations made of the intensity and polarisation of the scattered light for the widest range of angles of incidence and observation and for different physical conditions of the fluid. These results established a quantitative relationship between the surface-opalescence and the surface tension of liquids.

Though all the above-mentioned work had been done during the few months following the preliminary communication to 'Nature,' the complete results were not actually published till early in 1925 owing to Prof. Raman's absence on an American tour during 1924. Meanwhile, a purely mathematical paper by Gans,[3] dealing with the scattering of light

Mandelstam M., 'Annalen der Physik,' Vol. 41, p. 609 (1913).

R. Gans, 'Ann. der Physik,' Vol. 74, p. 231 (1924).

by a mercury surface, appeared in May, 1924. Our entirely independent work was communicated to the Proceedings of the Royal Society as a series of three papers. In Paper I[4] of the series, the case of metallic liquids was dealt with. In Paper II[5] the transparent liquids were considered. In Paper III[6] the effect of contamination (mono-molecular films of oleic acid) on the surface opalescence of water, the intensity of scattering by the surfaces of nearly thirty transparent liquids as compared to that of a water surface, and the special phenomena in the neighbourhood of the critical state were described.

Earlier in 1925, the present writer published some observations on the scattering of light by *solid* surfaces[7] like those of freshly split mica, of freshly cracked glass and of polished metals. In the case of metals, however, the observed intense scattering was due to the imperfect nature of the polished surfaces ; but later on, mica-gold contact surfaces were prepared by cathodic sputtering.[8] They were as good as a *liquid* mercury surface and showed a surface-opalescence much feebler than in the case of mercury.

Further observations on the increase of scattering by a clean water surface, when mono-molecular films of various organic compounds (solid and liquid) were allowed to spread on it, have been included in a recent paper by the writer[9] on the origin of camphor movements and allied phenomena.

It may be mentioned here that some recent measurements of the ellipticity of light reflected at the Brewsterian angle by the surfaces of a large number of pure transparent liquids

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[8] L. A. Ramdas, Proc. Ind. Assn. Sc., Vol IX, Part IV, p. 323 (1926).

[9] L. A. Ramdas, Proc. Ind. Assn. Sc., Vol. X, Part I, p. 1 (1926).

seem to throw some light on the nature of liquid surfaces. The thickness of the transition layer at the boundary, calculated by assuming Drude's theory, comes out to be of molecular dimensions. This result is also supported by calculating the displacement of a surface element against opposing surface-tension as a result of thermal or molecular agitation of the boundary as suggested in Paper I. These results have been discussed in another paper.

It is evident from the above that the subject has been extensively developed. In the following pages an attempt has been made to see how far the theory proposed by Gans in his first paper dealing with a mercury surface and in his very recent paper[10] dealing with transparent liquids, would explain the observed facts. Towards the end of the paper, the results of a more exact study of the scattering by the surface of liquid carbon-dioxide in the neighbourhood of the critical state are set forth in detail.

2. THEORY OF SCATTERING BY MERCURY SURFACE.

The theory proposed by Gans may be given briefly as below:—

A beam of light is incident on the surface of mercury ($z=0$). $x\ z$ is the plane of incidence. The roughness of the mercury surface (controlled by surface tension alone, neglecting the effect of gravity) gives rise to what may be called a disturbance field in addition to the electro-magnetic field which would exist if the surface were absolutely plane. Applying Maxwell's equations which hold for both the natural and the disturbance fields, with the boundary conditions (at the surface) $E_x = 0$ and $E_y = 0$ where E_x and E_y are the electric intensities parallel to the x and y axes. Gans finds that the disturbance field which is responsible for the scattered light is equivalent to a system of periodic magnetic di-poles of moment components $p_x . do$ and $p_y . do$ in a surface element do, with its axis $p_z = 0$. The radiation due to these periodic magnetic di-poles in a surface element do, in any direction is given by

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[10] R. Gans, 'Annalen der Physik,' Vol. 79, p. 204 (1926).

$$\frac{c}{4\pi} . \overline{h^2_\xi} \text{ and } \frac{c}{4\pi} \overline{h^2_\eta}$$

for the horizontal and vertical (*i.e.*) perpendicular to the horizontal and to the direction of observation) polarised parts where

$$(1) \qquad \overline{h^2_\xi} = \frac{2k\text{T}do}{\lambda \gamma^2 r^2} \frac{[\text{D} \cos a \sin \phi + \text{C}(\sin a \sin v - \cos \phi)]^2}{\sin^2 a + \sin v - 2 \sin a \sin v \cos \phi}$$

$$(2) \qquad \overline{h^2_\eta} = \frac{2\,k\,\text{T}\,do}{\lambda\,\gamma^2 r^2} \frac{[\text{D} \cos a \cos \phi + \text{C} \sin \phi]^2 \cos^2 v}{\sin^2 a + \sin^2 v - 2 \sin a \sin v \cos \phi}$$

and

$$(3) \qquad \overline{h_\xi \; h_\eta} = \frac{2\,k\,\text{T}\,do}{\lambda\,\gamma^2 r^2} \times [\text{D} \cos a \cos \phi + \text{C} \sin \phi]$$

$$\times \frac{[\text{D} \cos a \cos \phi + \text{C}(\sin a \sin v - \cos \phi)]}{\sin^2 a + \sin^2 v - 2 \sin a \sin v \cos \phi}$$

Here, C and D are the electric intensities of the incident wave in the plane of incidence and perpendicular to it respectively and are related to the intensity J_0 of the incident beam as,—

$$(i) \qquad \overline{\text{C}^2} = \overline{\text{D}^2} = \frac{4\pi}{c} . \text{J}_0 ; \quad \overline{\text{CD}} = 0.$$

when the incident light is unpolarised (natural),

$$(ii) \qquad \overline{\text{C}^2} = \frac{8\pi}{c} . \text{J}_0 ; \; \text{D} = 0$$

when the incident light is polarised at right angles to the plane of incidence and

$$(iii) \qquad \text{C} = 0, \; \overline{\text{D}^2} = \frac{8\pi}{c} . \text{J}_0 .$$

when polarised in the plane of incidence.

c=velocity of light,

a=angle of incidence,

v=the angle which the direction of observation makes with the normal to the surface of mercury,

ϕ=the azimuth of the plane of observation (*i.e.*) the plane containing the direction of observation and the normal to the surface) ; ϕ=o or 180° according as the direction of observation is on the reflection half or the incidence half of the plane of incidence.

k=Boltzmann's constant ($\frac{R}{N}$)

R—gas constant

N—Avogadro's number.

T—absolute temperature.

γ—surface-tension in dynes.

λ—wave-length of the incident light.

σ—the distance from *do*, the surface element illuminated by incident light.

Let us now put

$$\frac{c}{4\pi}\cdot\overline{h_{\xi}^{2}}=a_1$$

and

$$\frac{c}{4\pi}\cdot\overline{h_{\eta}^{2}}=a_2$$

$$\frac{c}{4\pi}\cdot\overline{h_{\xi}h_{\eta}}=a_{12}\,.$$

Then we have

(4) $$a_1 = R'[D\cos\alpha\sin\phi + C(\sin\alpha\sin v - \cos\phi)]^2$$

(5) $$a_2 = R'[D\cos\alpha\cos\phi + C\sin\phi]^2\cos^2 v$$

(6) $$a_{12} = R'[D\cos\alpha\sin\phi + C(\sin\alpha\sin v - \cos\phi)]$$
$$\times[D\cos\alpha\cos\phi + C\sin\phi]\cos v.$$

where

$$R' = \frac{}{4\pi}\cdot\frac{2kT.do}{\gamma\lambda^4 r^2}\times\frac{1}{\sin^2\alpha + \sin^2 v - 2\sin\alpha\sin v\cos\phi}$$

When the incident beam is plane polarised the scattered light is also plane polarised. If the intensity of the scattered light in any direction be A^2 and ψ the angle which the direction of vibration makes with the horizontal (as in figure), we have

$$A^2\cos^2\psi = a_1$$

$$A^2\sin^2\psi = a_2$$

and

$$A^2\sin\psi\cos\psi = a_{12}.$$

Now,

$$a_1 - a_2 = A^2(\cos^2\psi - \sin^2\psi)$$
$$= A^2\cos 2\psi$$
$$a_{12} = A^2\sin\psi\cos\psi.$$
$$= \tfrac{1}{2}A^2\sin 2\psi$$

so that

(7) $$\tan 2\psi = \frac{2a_{12}}{a_1 - a_2}.$$

We are thus able to find out both the intensity and direction of vibration of the scattered light when it is plane polarised (which is the case when the incident light is plane polarised in or at right angles to the plane of incidence).

CASE I.

When the incident light is polarised at right angles to the plane of incidence we have

$$\overline{C^2} = \frac{8\pi}{\;} \cdot J_0 \text{ and } D = 0.$$

Then,

$$(8) \qquad \begin{cases} a_1 = 2R(\sin \alpha \sin v - \cos\phi)^2, \\ a_2 = 2R(\sin^2\phi \cos^2 v) \text{ and} \\ a_{12} = 2R(\sin \alpha \sin v \cos \phi)\sin \phi \cos v. \end{cases}$$

where R is now given by

$$(9) \qquad R = \frac{2kTJ_0 do}{\gamma . \lambda^2 r^2} \times \frac{\;}{\sin^2\alpha + \sin^2 v - 2 \sin \alpha \sin v \cos \phi}$$

The intensity of the scattered light is

$$I = a_1 + a_2.$$

$$(10) \qquad = \frac{4kTJ_0 do}{\gamma \lambda^2 r^2} \cdot \frac{(\sin \alpha \sin v - \cos \phi)^2 + \sin^2\phi \cos^2 v}{\sin^2\alpha + \sin^2 v - 2 \sin \alpha \sin v \cos \phi}$$

and for the direction of vibration we have,

$$(11) \qquad \tan 2\psi = \frac{2a_{12}}{a_1 - a_2} = \frac{2(\sin \alpha \sin v - \cos \phi)\sin \phi \cos v}{(\sin \alpha \sin v - \cos \phi)^2 - \sin^2\phi \cos^2 v}$$

CASE II.

When the incident light is polarised in the plane of incidence, we have,

$$C = 0 \quad \text{and} \quad \overline{D^2} = \frac{8\pi}{\;} \cdot J_0$$

so that

$$(12)\qquad \begin{cases} a_1 = 2R\cos^2\alpha\sin^2\phi \\ a_2 = 2R\cos^2\alpha\cos^2\phi\cos^2 v \\ a_{12} = 2R\cos^2\alpha\sin\phi\cos\phi\cos v\ldots \end{cases}$$

$$\therefore \qquad I = a_1 + a_2.$$

$$= 2R\cos^2\alpha(\sin^2\phi + \cos^2\phi\cos^2 v)$$

$$= 2R\cos^2\alpha(1 - \cos^2\phi + \cos^2\phi\cos^2 v)$$

$$= 2R\cos^2\alpha(1 - \cos^2\phi\sin^2 v)$$

$$(13)\qquad \frac{4kTJ_0 d0}{\gamma\lambda^4 r^2}\ \frac{(1-\cos^2\phi\sin^2 v)\cos^2\alpha}{\sin^2\alpha + \sin^2 v - 2\sin\alpha\sin v\cos\phi}$$

and from (7)

$$\tan 2\psi = \frac{2\cos^2\alpha\sin\phi\cos\phi\cos v}{\cos^2\alpha(\sin^2\phi - \cos^2\phi\cos^2 v)} = \frac{\sin 2\phi\cos v}{\sin^2\phi - \cos^2\phi\cos^2 v}$$

Equations 10, 11, 13 and 14 may now be used for calculating the intensity and direction of vibration of the scattered light in various interesting cases.

3. COMPARISON WITH EXPERIMENTAL RESULTS.

CASE I.

A. *Normal incidence of polarised light, vibrations in XZ plane.*

Putting $\alpha = 0$ in equations 10 and 11,

$$(15)\qquad I = M\left[\frac{\cos^2\phi + \sin^2\phi\cos^2 v}{\sin^2 v}\right]$$

where

$$M = \frac{4kTJ_0 do}{\gamma\lambda^4 r^2}$$

$$\tan 2\psi = -\frac{2\cos\phi\sin^2\phi\cos v}{\cos^2\phi - \sin^2\phi\cos^2 v}.$$

$$(16)\qquad = \frac{-\sin 2\phi\cos v}{\cos^2\phi - \sin^2\phi\cos^2 v}$$

The following table shows the values of $\frac{1}{M}$ and ψ calculated for various azimuths and altitudes. Diagram I_a shows these calculated values and compares very well with Diagram I_b which shows the experimental results already described in Paper I (Raman and Ramdas, Proc. Roy. Soc., Vol. 108, A, 1925, p. 565).

TABLE I.

ϕ	v	Intensity/M	tan 2 ψ	ψ.
90°	90°	·0	0	0 (horizontal vibrations)
	75°	·072	0	do
	60°	·333	0	do
	40°	1·400	0	do
0 or 180°	90°	1·000	(−ve before vanishing)	90° (vertical)
	75°	1·072	0	do
	60°	1·334	0	do
	40°	2·421	0	do
45°	90°	0·500	−ve before vanishing	90° (vertical)
	75°	0·570	− ·5549	90°−15°
	60°	0·840	−1·3340	90°−27°
	40°	1·920	−12·8800	90°−43°
135°	90°	0·500	+ve before vanishing	90° (vertical)
	75°	0·570	+ ·5549	90°+15°
	60°	0·840	+ 1·3340	90°+27°
	40°	1·920	+12·8800	90°+43°

An inspection of Table I and figures I_a and I_b shows that, as mentioned in Paper I, the scattered light is of greatest intensity in the azimuth containing the electric vector of the incident waves and of minimum intensity perpendicular to it. In the latter case $\phi=90^\circ$, when the direction of observation is

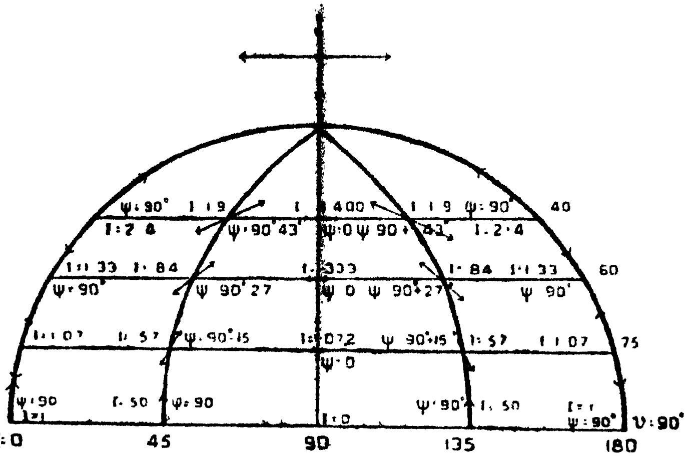

FIG. I_a *(theoritical)*

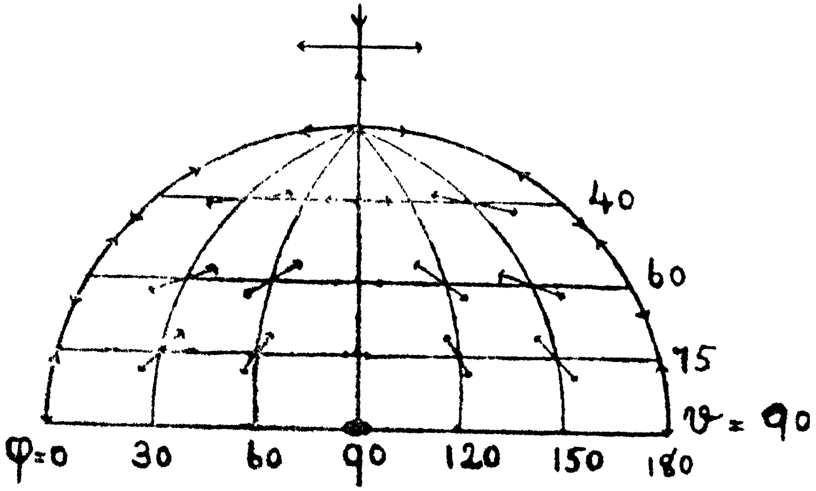

FIG. I_b (*experimental*)

parallel to the surface *i.e.*, $v=90^\circ$, the intensity is zero. In this azimuth for decreasing values of v the intensity increases but the direction of vibration remains horizontal. At azimuths $\phi=45°$ and $\phi=135°$, however, the electric vector turns round anti-clock-wise and clock-wise respectively from the horizontal and becomes quite vertical in the plane of incidence. Fig. I_a agrees with the experimental results. (See Fig. I_b.)

B. *Nearly grazing incidence of polarised light (vibrations in the plane of incidence and $\alpha=80°$).*

The following table shows the values of intensity (I/M) and ψ calculated from the expressions (10) and (11). Fig. II_a represents these values and Fig. II_b shows the experimental results obtained for this case. (See paper I.)

TABLE II.

ϕ	v	$\frac{\text{Intensity.}}{\text{M}}$	tan 2 ψ	ψ
0	90°	1	(−ve before vanishing.)	90° (vertical).
	70°	2·8	do.	do.
	60°	1·53	do.	do.
	45°	1·12	do.	do.
	0°	1·02	do.	do.
180°	90°	1·0	do.	$(\pi+90°)$.
	70°	1·0	do.	vertical.
	60°	1·0	do.	do.
	45°	1·0	do.	do.
	0	1·02	do.	do.

TABLE II—*Contd.*

ϕ	v	$\frac{\text{Intensity.}}{\text{M}}$	tan 2 ψ	ψ
30°	90°	·054	+0(2$\psi \gtrless$ 180)	90° (vertical).
	77°	...	±∞	90° + 45°
	75°	·002	−2·33	90° + 57°
	61°33′	...	∓0	90° + 90° (horizontal).
	60°	·258	+ ·11	180° + 3°
	40°	·700	+1·827	180° + 30°40′
	25°	·952	+135·0	180° + 45°.
45°	90°	·137	+0(2$\psi \gtrless$ 180)	90° (vertical)
	75°	·167	+3·412	90° + 36°37′
	71°5′	...	±∞	90° + 45°
	60°	·285	− ·0725	90° + 88°
	45°52′	·515	∓0	180° horizontal.
	25°	·882	+ ·1864	180° + 5°17′
90°	90°	·492	+0(2$\psi \gtrless$ 180)	90° (vertical)
	75°	·511	+ ·5878	90° + 15°13′
	60°	·568	+1·756	90° + 30°21′
	45°	·670	−65·66	90° + 45°50′
	25°	·870	−1·163	90° + 65°21′
135°	90°	·85	+0(2$\psi \gtrless$ 180)	90° (vertical)
	75°	·87	+ ·2234	90° + 6°18′
	60°	·93	+ ·4779	90° + 12°46′
	45°	·90	+ ·8156	90° + 19°36′
	25°	·96	+1·692	90° + 29°42′

It is indeed remarkable that all the complex effects observed by us in this case (Paper I) are faithfully reproduced from theory. The turning round, through nearly two right angles, of the electric vector at azimuth 45° is very clear from the above table and Fig. II_a. The surprising observation that more light is scattered in the backward direction, *e.g.*, $\phi=90^\circ$ to 180°, than in the forward direction $\phi=90^\circ$ to $\phi=0$, is also indicated by theory. Fig. II_a compares quite well with Fig. II_b (experimental).

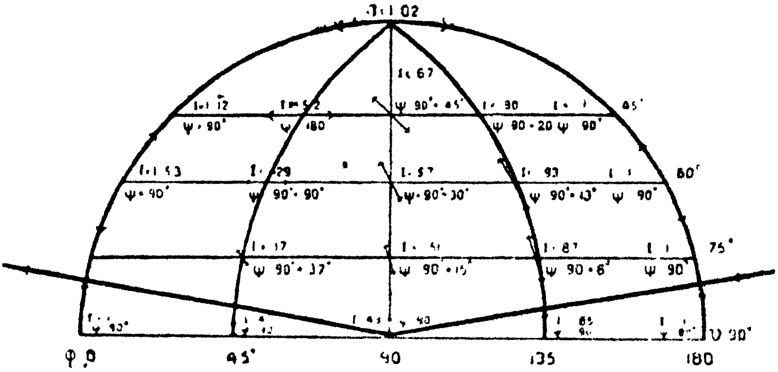

FIG. II*a* (*theoretical*)

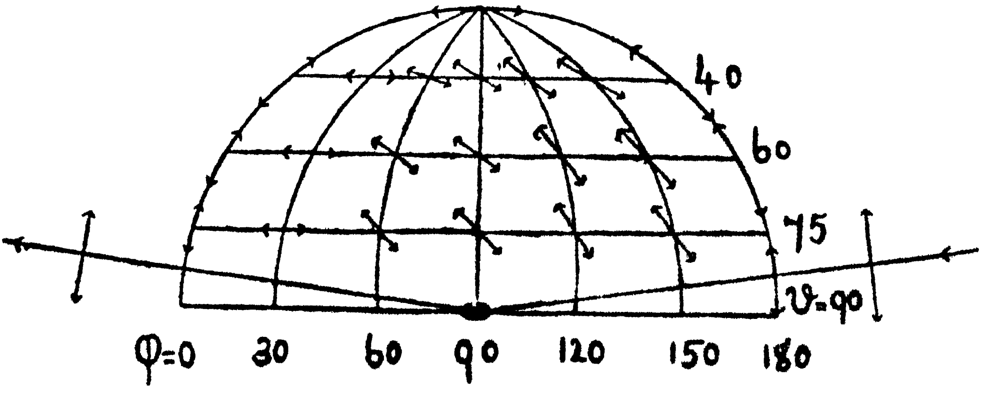

FIG. II *b* (*experimental*)

CASE II.

Incident light is polarised in the plane of incidence (i.e., vibrations perpendicular to plane of incidence and always horizontal). With the help of equations 13, 14, I/M and ψ for $a=80^\circ$ (as before) have been calculated. (See Table III.)

TABLE III.

ϕ	v	Intensity M	tan 2ψ	ψ
0	90°	0	0	0
	70°	1·733		
	60°	·533		
	45°	·190		
	0	·031	Vibrations	horizontal.
180	20°	·015		
	45°	·005		
	75°	·0005		
	90°	Zero.		
45°	90°	·026	+0	90° (vertical)
	60°	·037	+1·334	90° + 26°33′
	45°	·047	+2·829	90° + 35° 15′
	30°	·050	+6·928	90° + 40° 54′
90°	90°	·015	+0	90° (vertical).
	45°	·020	do.	do.
	30°	·025	do.	do.
135°	90°	·0045	$-0(2\psi \geqslant 180)^\circ$	90° (vertical).
	60°	·0064	−1·33	90° − 26° 53′
	45°	·0092	−2·83	90° − 31° 15′
	30°	·0130	−6·90	90° − 40° 54′

The above values are represented in Fig. III, and show that the turning round at $\phi=45^\circ$ is less than in Fig. II, and that the intensity of the scattered light in all directions is much smaller than in the previous case. The intensity is appreciable in the forward direction ($\phi=0$ to 90°), but is almost negligible for $\phi=90^\circ$ to 180°. The direction of vibration is horizontal in the plane of incidence at all angles of observation. These results bear out the experimental observations (See paper I, pp. 566-7.)

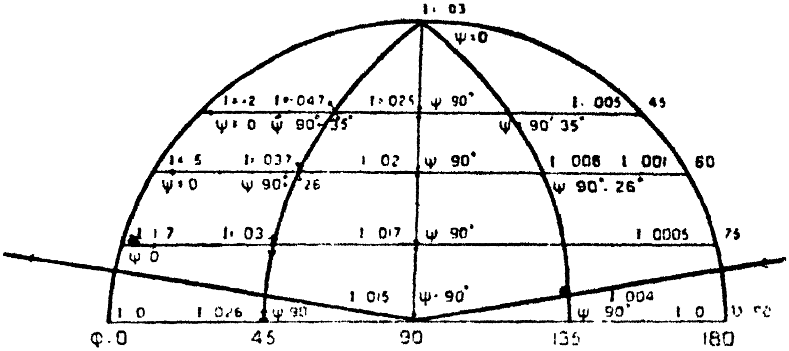

FIG. III.

CASE III.

We now come to the remarkable effects observed when the angle of incidence is 45° and the incident vibration makes an angle $\theta=45^\circ$ with the plane of incidence. In this case the scattering is not symmetrical with respect to the plane of incidence, but is much more intense on one side of it than on the other. There may be quite strong scattering in azimuths from 45° to 135° and little or no scattering in azimuths from 225° to 315° on the other side. These results can be easily explained from theory. For, in equations (1) and (2), we have, if the electric intensity in the incident waves is E, $C=+E\cos\theta$ always, while $D=\pm E\sin\theta$ according as the angle made by the direction of E is ± 45°. Substituting in 1 and 2 we have in one case the square of the sum and in the other case the square of the difference of two terms in the expression for the intensity of the scattered light.

Absolute Intensity of the Scattered Light.

We can calculate the intensity of the scattered light in a direction $\nu = 50°$ for normal incidence of unpolarised (natural) light putting $\frac{J_o\, dO}{r^2} = 1$, *i.e.*, when the incident light has an intensity 1, and $\frac{dO}{r_2} = 1$, *i.e.*, for unit solid angle. The expression for the intensity is

$$I = \frac{2kT}{\gamma \times \lambda^4} \times \frac{1 + \cos^2 \upsilon}{\sin^2 \upsilon}$$

For $\lambda = 5500$ and $\upsilon = 50°$, when $\gamma = 547$ dynes 1 cm

$$\underline{\underline{I = 1{\cdot}2 \times 10^{-7}}}$$

The experimental value (See paper I) is

$$\underline{\underline{1 = {\cdot}91 \times 10^{-7}}},$$

in good agreement with the above calculated value.

The calculations made in the previous sections show that the general features of the distribution of intensity in directions sufficiently removed from the reflected beam and of the polarisation effects are in agreement with the observations made in paper I. It must be pointed out, however, that Gans' theory indicates a very rapid increase in the intensity of the scattered light as one approaches the direction of regular reflection. This is *not* borne out by both visual observation and actual photographic photometry of the opalescent spot for decreasing values of v. The images of the spot obtained for equal exposures do not show *any increase* in intensity on approaching the reflected light when *unpolarised* light is incident normally, whereas the enormous increase indicated by Gans' theory may be noted from the following table.

v.	Intensity/M
90°	1·00
60°	1·66
30°	7·00
15°	29·00

4. THE SCATTERING OF LIGHT BY THE SURFACES OF TRANSPARENT LIQUIDS.

In his second paper Gans has discussed the theory of light scattering by the interface ($z=0$) between two fluids (both liquids or one liquid with its own vapour above). The problem is theoretically more difficult as one has to consider reflection as well as refraction at the boundary which is not a conductor in the present case. From essentially similar considerations modified, however, by the altered boundary conditions in the present instance, Gans arrives at the expressions for intensity set down below.

To make matters clearer let us call the plane containing the direction of observation and the normal to the surface the plane of observation. The intensity of the scattered light observed at any angle in this plane may be considered as the sum of two intensities I_s and I_p, where I_s is due to the electric vector at right angles to the plane of observation and I_p is due to the electric vector in the plane of observation.

Case I, The electric vector in the incident beam at right angles to the plane of incidence.

In the upper medium we have

$$(17)\quad \begin{array}{l}\text{for}\\ z>0\end{array}\quad \begin{aligned} I_1 &= R\left(\frac{\cos\delta}{\cos\delta+n\cos\delta'}\right)^2\left(\frac{\cos\phi\cos v}{\cos v+n\cos v'}\right)^2\\ I_2 &= R\left(\frac{\cos\delta}{\cos\delta+n\cos\delta'}\right)^2\left(\frac{\cos v'\cos v\sin\phi}{n\cos v+\cos v'}\right)^2\end{aligned}$$

where

$$(18)\qquad R=\frac{4kT J_{ee}\, do}{r^2\,\gamma\,\lambda^2}(n^2-1)^2\times\frac{1}{\sin^2\delta+\sin^2 v-2\sin\delta\times\sin v\cos\phi}.$$

and n is the refractive index of the second medium with respect to the first (*i.e.*, the medium into which the light enters first).

Then we have

$$n\sin\delta'=\sin\delta,\quad \delta \text{ being the angle of incidence}$$

and

$$n\sin v'=\sin v.$$

The other symbols have the same significance as before.

For the lower medium (λ in R is the wave-length in the lower medium) we have

$$(19)\quad z<0\quad \begin{aligned} {}' &= Rn\left(\frac{\cos\delta}{\cos\delta+n\cos\delta'}\right)^2\left(\frac{\cos v'\cos\phi}{\cos\delta+n\cos v'}\right)^2\\ {}' &= Rn\left(\frac{\cos\delta}{\cos\delta+n\cos\delta'}\right)^2\left(\frac{\cos v'\cos v\sin\phi}{n\cos v+\cos v'}\right)^2\end{aligned}$$

For the case of total reflection we have to substitute, in (17) and (19),

$$\frac{\cos^2\delta}{1-n^2}\quad\text{for}\quad\frac{\cos^2\delta}{(\cos\delta+n\cos\delta')^2}.$$

Case II, Electric vector in the incident light is in the plane of incidence.

$$(20)\quad z>0\quad \begin{cases} I_s=R\left(\dfrac{\cos\delta\cos v}{n\cos\delta+\cos\delta'}\right)^2\left(\dfrac{\cos\delta'\sin\phi}{\cos v+n\cos v'}\right)^2 \\[2ex] I_p=R\left(\dfrac{\cos\delta\cos v}{n\cos\delta+\cos\delta'}\right)^2\left(\dfrac{\cos\delta'\cos v'\cos\phi-\sin\delta\sin v}{n\cos v+\cos v'}\right)^2 \end{cases}$$

$$(21)\quad z<0\quad \begin{cases} I'_s=Rn\left(\dfrac{\cos\delta\cos v'}{n\cos\delta+\cos\delta'}\right)^2\left(\dfrac{\cos\delta'\sin\phi}{\cos v+n\cos v'}\right)^2 \\[2ex] I'_p=Rn\left(\dfrac{\cos\delta\cos v'}{n\cos\delta+\cos\delta'}\right)^2\left(\dfrac{\cos\delta'\cos v\cos\phi+\sin\delta'\sin v}{n\cos v+\cos v'}\right)^2 \end{cases}$$

We may now proceed to examine how far these expressions would explain the observed distribution of intensity and polarisation in the case of transparent liquids at ordinary temperatures (*i.e.*, far below the critical temperature).

(*a*) Whereas in the case of the mercury surface the intensity is more or less uniform in all directions, when the incident light is unpolarised, in the case of the transparent liquids most of the scattering is confined to the neighbourhood of the reflected and refracted beams, the intensity diminishing very rapidly as one goes away from these directions. The intensity is practically zero at azimuths $\phi=90^\circ$ to $\phi=180^\circ$.

The distribution of intensity in various azimuths for 0 to 90°, keeping the angle of observation v=critical angle, when the angle of incidence is nearly 40° from below, has been measured experimentally for methyl alcohol (see paper II, Raman and Ramdas, Proc. Roy. Soc., Vol. 109. A., p. 150, 1925). The calculated values for this case are compared with these values in the following table (the absolute values of the intensity being given). Both indicate the rapid falling off of the intensity for increasing values of ϕ from $\phi=0$. It may be noted, however, that the theoretical values show a *too* *rapid* falling off of the intensity. The defect of the theory is similar to the one pointed out at the end of the previous section in the case of mercury. Both sets of values, however, indicate that in azimuths larger than 90° there is very little scattering to be observed unless the incidence is nearly normal.

TABLE IV (UNPOLARISED LIGHT INCIDENT).

ϕ	1×10^6 Calculated.	1×10^6 observed.
0°	17·8	3·1
10°	7·9	2·4
20°	2·9	1·1
30°	1·3	·93
40°	·72	·85
50°	·43	·68
60°	·28	·60
75°	·16	·35
90°	·12	·23

(*b*) As the angle of observation v in a fixed plane of observation, $\phi=$constant, is decreased from 90°, the intensity of the opalescent spot at the surface goes on increasing and attains a maximum value suddenly, at $v=$critical angle for the medium, and then slowly diminishes in intensity. The intensity may increase again if, for diminishing values of v the direction of the refracted or reflected beam is approached. In the following table the intensity for various values of v has been calculated for the case of normally incident unpolarised light (from above) in the case of methyl alcohol. The values show a maximum value at the critical angle the further increase after a fall being due to the reflected beam being approached. The values given are I/R^1, where $R^1=\frac{2KT(n^2-1)^2}{9\lambda^4}$.

TABLE V.

v	Intensity /R.[1]
90°	0
75°	·2
60°	1·28
50°	1·60
47° 42′ (critical angle)	1·83
40°	1·30
15°	9·50
0	(refracted beam).

(*c*) As regards the law of polarisation of the scattered light it may be mentioned that the vibrations in the scattered light are simply related to those in the incident light. This may be readily understood from a discussion of the case in which polarised light is incident normally on the liquid surface and the direction of observation is nearly *parallel* to the liquid surface and to the direction of vibration in the incident light. The intensity of the scattered light is found to be practically zero. In a direction perpendicular to the vibrations of the incident light, however, the intensity is very strong. This law of polarisation is the same as for the internal (Rayleigh) scattering. *The case of mercury, which is a metal, is evidently the exception to this rule.*

(*d*) The scattering power of the surfaces of various pure liquids for the simple case of normal incidence of unpolarised light from below and observation at the critical angle from below, has been measured in terms of the scattering power of a water surface (see paper III, Raman and Ramdas, Proc. Roy. Soc., A, Vol. 109, p. 272, 1925). We can, therefore, compare these values with those calculated with the help of expressions (17), (19), (20), (21). The two sets of values are given in Table VII below. The agreement between the observed and the calculated values is fair. The dependence of the intensity on the surface tension and refraction index is clearly indicated.

TABLE VII.

Substance.	γ	n_F	Intensity (water = 1) Calculated.	Intensity (water = 1) observed.
Water	72	1·336	1·0	1·0
	Paraffins and	*Unsaturated Hydro-Carbons*		
Hexane	16·34	1·374	5·8	8·5
Octane	20·00	1·396	5·5	7·8
	Chlorides.			
Ethylene chloride ...	30·1	1·445	4·9	3·8
Chloroform	25·3	1·446	5·9	6·3
Carbon-tetra chloride ...	24·6	1·462	6·6	12·6
Si cl_4	15·8	1·420	8·0	7·4
	Fatty	*Acids.*		
Formic acid	85·75	1·372	2·6	4·6
Acetic acid	23·50	1·373	4·0	4·9
Propionic acid	26·60	1·387	3·8	5·8
Butyric acid	26·70	1·397	4·1	6·3
	Oxides.			
Ethyl ether	15·27	1·352	5·3	7·4

TABLE VII—*contd.*

Substance.	γ	n_r	Intensity (water = 1) Calculated.	Intensity (water = 1) observed.
	Alcohols.			
Methyl Alcohol ...	23·00	1·329	3·0	4·0
Ethyl Alcohol ...	22·00	1·363	4·0	5·2
i-propyl	21·34	1·380	4·6	7·2
Butyl	24·40	1·400	4·6	7·4
i-butyl	22·80	1·397	4·8	9·3
Allyl	23·15	1·419	5·5	7·8
Benzyl	39·70	1·547	6·43	10·0
	Esters.			
Ethyl Formate ...	22·00	1·359	3·9	5·2
Propyl formate ...	22·20	1·379	4·4	7·4
Propyl acetate	22·00	1·385	4·6	5·6

5. SURFACE-PHENOMENA IN THE NEIGHBOURHOOD OF THE CRITICAL STATE.

We have been hitherto considering the scattering of light by liquid surfaces at ordinary temperatures, *i.e.*, far below the critical temperature. As mentioned before, the scattering is inversely proportional to the surface tension and therefore increases enormously as the critical temperature is approached and therefore the surface tension also diminishes rapidly to zero. A general description of the phenomenon for the case of liquid Co_2 approaching its critical temperature has been already given in Paper III (Raman and Ramdas, Proc. Roy. Soc., A., Vol. 109, p. 272, 1925) along with illustrations showing the enormous increase of the intensity of the opalescent spot close to the critical temperature.

Since then the writer undertook a more detailed study of the phenomenon of surface-scattering in the neighbourhood of the critical temperature by liquid Co_2. The actual variation of the intensity of scattering with the temperature and various other interesting facts regarding the nature of the fluid at and near the critical temperature have been noted. These results are discussed below. The intensity data obtained have been compared with the values calculated from theory.

Experimental Arrangements.

The carbon dioxide had been sealed off in a thick-walled bulb for work on the internal scattering of light at high pressures by Raman and Ramanathan. While preparing the bulb, sufficient care had been taken by them to evacuate the bulb before and while filling it with solid Co_2 under liquid air. The bulb had been kept immersed in liquid air and the evacuating pump kept in action while sealing off the bulb at the stem. The percentage of impurity may therefore be expected to be very small indeed.

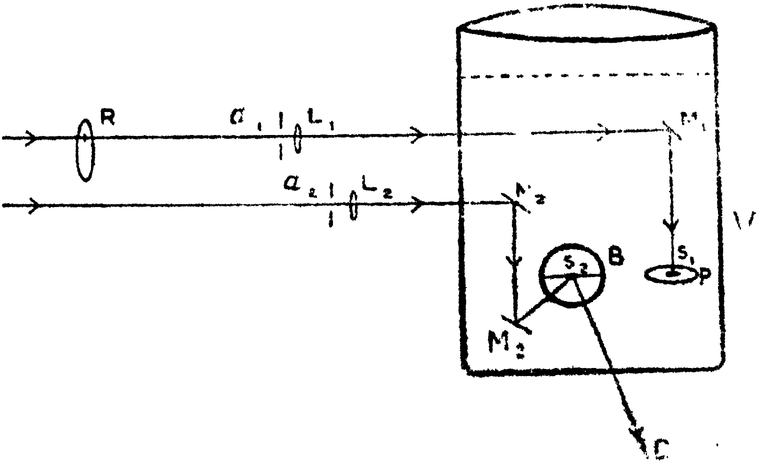

Fig. IV

The actual arrangements used for the work may be seen in fig. IV. V is the big glass vessel filled with clean water in which the system of mirrors M_1, M_2, and M_3 for adjusting the necessary beams of light, the carbon dioxide bulb B and the slab of plaster of paris P are kept. L_1 and L_2 are a Zeiss and a Ross Camera lens respectively, provided with adjustable apertures a_1 and a_2. R is a rotating sector with a small aperture (angular) having a reducing factor as small as $\frac{1}{850}$ and adjusted so as to reduce the intensity of light passing through the Zeiss lens L_1.

The vessel V was placed in a big wooden box provided with two windows, one to admit the two beams of sun-light $L_1 M_1$ and $L_2 M_2$ into the vessel and another for observation in a direction perpendicular to $L_1 M_1$. The interspace was covered with glass-wool for adequate heat-insulation.

A broad beam of sun-light was reflected into the dark room and the two beams $L_1 M_1$ and $L_2 M_2$ condensed into the tank. They were then reflected as required by the small adjustable mirrors M_1, M_2, M_3 so as to be focussed at S_1 from above on P and at S_2 on the surface of the liquid CO_2 from below. On trial it was found that, after the suitable adjustment of L_1 and L_2, any changes in the sizes of the apertures a_1 and a_2 did not vary the sizes of the focal spots S_1 and S_2. The equivalent aperture values of L_1 and L_2 were determined by putting another slab of plaster of Paris at S_2 and adjusting a_1 and a_2 for equality in the intensity of S_1 and S_2 after removing the rotating sector R. In order to avoid any stray light, all extra illumination was carefully cut off by suitable screens in front of L_1 and L_2, by blackening the outside of the glass vessel V and by reducing the apertures a_1 and a_2 as far as possible.

The beam reflected down by M_2 vertically and again reflected up by M_3, was incident on the surface of the liquid

CO_2 in B at about 45°, the plane of incidence being so adjusted as to coincide with the plane of observation at right angles to the horizontal beam L_4 M_2. On viewing the surface of the liquid from below at an angle equal to the critical angle, the opalescent spot could be observed distinctly at the surface. The spot was much brighter than the blue tracks in the liquid and in the vapour above due to internal scattering. The plaster of Paris P was so adjusted that the spot S_1 also could be viewed simultaneously and nearly in the same plane of observation. The two spots could be adjusted to have equal intensity by running the sector R and adjusting the aperture a_1 whose readings could be easily read off. The intensity measurements were taken in this way with a red screen in front of the eye. The screen helped to cut off most of the internal scattering so long as it was blue.

Arrangements for maintaining and adjusting the temperature.

In all measurements in the neighbourhood of the critical temperature of a substance it is very essential to be able to control the temperature of the substance (*i.e.*, of the bath in which it is kept) and maintain it constant when necessary for a sufficient length of time. In the present work it was possible to control the temperature over the range from 30·5°C. to 31·5°C. as the mean temperature of the room was about 31°C. during most of the days the experiment was performed (May, 1926). The water in the tank was continuously stirred and slight alterations in temperature made by evaporation* from the tank by working a fan for a few minutes *for lowering* or adding a small quantity of slightly warmer water *for raising* the temperature.

For reading the temperatures a very carefully calibrated Beckmann thermometer was used. The calibration was done by finding out the melting point of hydrated sodium sulphate (Na_2SO_4, $10H_2O$) *i.e.*, 32·383°C. The corresponding reading in the Beckmann thermometer was 1·014° (Beckmann readings increase for fall of temperature).

Optical phenomena near the Critical Temperature.

After making the above arrangements the following observations were made when (*a*) the temperature was raised to the critical temperature and (*b*) the temperature was lowered to the critical temperature. In both cases the necessary alterations of the temperature were made slowly and in steps so that the bulb had ample time to attain the temperature indicated by the thermometer.

(*a*) *Rising temperature.*

The temperature was initially lower than the critical temperature by three or four degrees. Placing the eye in the plane of incidence, above the reflected light, at the critical angle, the opalescent spot at the surface (*i.e.* where the tracks in the liquid and vapour meet) could be seen very distinctly and much whiter and more intense than the tracks due to the internal scattering. On increasing the temperature slowly and stopping at intervals (stirring all the while) the surface scattering was found to increase in intensity. The critical angle, at which the spot was always viewed, continuously increased owing to the diminution of the refractive index of the liquid carbon dioxide with respect to its vapour above. The scattering by the surface increased very rapidly while the temperature rose above 30°C. in steps of ·01°C. To ensure equality of temperature of the liquid and vapour, the bulb was also vigorously shaken and allowed to rest before taking any observation while making these observations, the corresponding diminution in the intensity of the reflected beam was also studied by catching it on a white screen. The intensity of the scattered light rose to a maximum at 31·131°C. and at the same temperature the reflected beam also completely vanished, the surface of the liquid being evidently too rough to regularly reflect any light. When the temperature was further raised ever so little, the surface ceased to be sharp and the strong interfacial opalescence between liquid and vapour began to extend over a definite thickness depending on the rise of temperature above 31·131°C. The thickness of the transition layer could not be diminished or increased perceptibly by any amount of shaking or waiting. One has at this stage, three layers as it were, a liquid phase at the bottom, a vapour phase at the top and a thin cloudy layer at the interface. On further raising the temperature, this thin layer at the surface assumed thicknesses of increasing value until finally at about 31·377°C. it filled the whole bulb leaving a uniform intense track without any trace of the liquid phase. It may be mentioned here that the surface-scattering up to 31·131°C. is a real surface phenomenon confined mostly to the neighbourhood of the reflected beam, whereas the scattering by the thick surface layers above this temperature is more like internal scattering and visible equally well in all directions.

The above observations were repeated any number of times with similar results. The temperature 31·131° C. beyond which the surface ceased to reflect any light and began to thicken into a definite layer could be obtained over and over again. If the heating was proceeded with too rapidly the cloud effects at the surface could be obtained at temperatures lower than 31·131°C., but were dissipated in a short time as soon as temperature equilibrium was attained. If the heating was slow and in short stages, the premature formation of the cloudy layer at the surface could be avoided completely till 31·131°C. was reached. The white scattering above this temperature by the thick transition layer is probably a kind of transition effect between pure surface scattering and the more familiar internal or body scattering. This requires more careful study.

(*b*) *Falling temperature.*

In this case the changes observed are not so complex. The temperature was initially 32°C. The track of the beam of light was bluish and did not show any non-uniformity of intensity. As the temperature was lowered very slowly, and kept steady while making observations at intervals, the track slowly got whiter and the intensity was found to increase rapidly, but without any tendency of the fluid to separate into two layers, *viz.*, liquid and vapour, even below 31·377°C. (at which the liquid phase disappeared with 'rising temperature'). The body scattering continued to increase to a maximum at 31·137°C. At and below this temperature up to 31·131°C. the track began to get distinctly cloudy and reddish owing to the very rapid weakening of the incident light by the intense scattering by the medium. On keeping the temperature steady, the cloudiness began to clear up and the liquid meniscus appeared. The temperature 31·131°C. seems therefore to be a very characteristic temperature of the liquid, *i.e.*, one at which its surface of separation ceases tc be sharp, or tends to disappear (the liquid phase still persisting) for 'rising temperature' and at which the liquid phase reappears for 'falling temperature'. As soon as the liquid layer was formed, the scattering throughout the medium was bluer than before and the strong surface scattering could be observed in the plane of incidence. Further reducing the temperature, the surface-opalescence continuously diminished in intensity from its maximum value at 31·131°C. The existence of only a single phase for *falling temperature* above 31·131°C. may be due to the liquid and vapour phases (which are separated by the transition layer at the surface) for *rising temperature* being thoroughly mixed up so as to form something like a stable emulsion.

In fact, critical opalescence (internal) which has been studied experimentally by Keesom,[11] Andant[12] and Bhattacharya[13] and theoretically by Ornstein and Zernike[14] may be considered from an entirely different point of view. The intensity of the opalescence becomes proportional to the inverse square of the wave-length, as has been shown by the measurements of the above authors, in the neighbourhood of the critical temperature. We know already that surface scattering also obeys the inverse square law. Critical opalescence may, as well, be a complex effect, *viz.*, the scattering by the surfaces of innumerable droplets. This suggestion with regard to critical opalescence requires further exact experimental tests.

The weakening of the incident beam owing to scattering by the medium in the neighbourhood of the critical temperature has been measured. The measurements show that in accordance with the observations described above, the absorption is a maximum at *31·131*°C. In fact intensity measurements of the scattered light are of no value above this temperature as it is difficult to correct for the absorption by the layer through which one has to observe the track. Absorption measurements, on the other hand, are much easier to make and give the actual amount of light scattered by the medium in other directions. It may be pointed out here that Bhattacharya's values of the intensity of scattering above this temperature are too low on this account and the maxima of his intensity curves ought to be much higher still. The table below shows the comparative values of the transmitted intensity at different temperatures.

[11] Keesom; Ann. der Physik (1911).

[12] Annales de Physique, 2, 1924.

[13] Proc. Ind. Asn. Science Vol. VIII, Part IV, p. 277.

[14] Proc. Roy. Soc. Amsterdam, Part I, Vol. XVII, 1914.

Critical temperature of CO_2, as determined by previous workers:—

T_c	Observer
31·35°C.	Amagat (1892).
31·40°C.	Chappuis (1894).
30·98°C.	Keesom (1903).
31·10°C.	Dorsman (1908).
31·00°C.	Cordoso and Bell (1912).

The divergent values obtained are evidently due to ordinary visual observation. The optical method described in the present paper enables one to see critical phenomena in detail.

TABLE VIII.

Temperature.	Intensity of transmitted beam (green).
31·50°C	1·00
31·250	0·53
31·180	0·48
31·160	0·29
31·150	0·095
31·127	no clear transmission 0·20 (after reappearance of liquid).
31·117	0·75
31·107	0·78
31·087	0·85

(c) Intensity of surface scattering.

The intensity measurements were made for 'falling temperature' below 31·151°C. Measurements showed that the intensity of the scattering by the surface below this temperature was the same for both

A red filter was placed in front of the eye while taking the measurements. The values obtained have been given in Table IX where the theoretical values obtained from Gans' equations suitably modified, have also been given for comparison. For calculating the values, the refractive indices of the liquid with respect to the vapour are required. They were calculated from the indices of the vapour and liquid obtained separately from density data by using the Lorenz-Mossotti formula,

$$\frac{n^2-1}{n^2+2}=k\rho$$

where k is a constant and ρ is the density. For the values of the surface tension Verschaffelt's experimental values were plotted and values near the critical temperature obtained by extrapolation, the curve meeting the temperature axis at 31·131°C. The extrapolated values agreed with the values calculated from Mc. Leod's expression,

$$\gamma=C(\rho_l-\rho_v)^4,$$

where C is a constant and ρ_l and ρ_v are the densities of the liquid and the vapour respectively, except very near the critical temperature *i.e.*, above 30·5°C.

TABLE IX.

Temperature	γ in dynes/cm.	Intensity × 10^6 calculated.	Intensity × 10^6 observed.
31·10	·00015	3200	3000
31·05	·00060	990	1100
31·00	·0012	600	500
30·80	·0032	300	270
30·60	·009	150	120
30·40	·027	120	90
30·20	·035	100	70
30·00	·049	90	60

The agreement between the observed and calculated values is striking. Remembering that in the case of substance like methyl alcohol at a temperature much lower than the critical temperature, the calculated values of the intensity in the plane of incidence and in the neighbourhood of the reflected light, are too large; one may conclude that the theory holds better for surfaces in the neighbourhood of the critical temperature when the roughness of the surface is so large that most of the scattering is confined to the neighbourhood of the refracted and reflected rays.

6. SUMMARY AND CONCLUSION.

(1) The scattering of light by the surface of metallic mercury and a large number of transparent liquids was observed and studied in detail. These results, already published, are now compared with the theory proposed by R. Gans.

(2) In the case of mercury most of the intricate polarisation and intensity-distribution effects, when the incident light is polarised, are also indicated by theory, but, whereas observation shows a more or less uniform distribution of the intensity, when unpolarised light is incident, the calculated values show too rapid an increase in the intensity of the scattered light as the reflected beam is approached.

(3) For transparent liquids the main features of the scattered light are also shown by the theory. For example

(*i*) the confinement of most of the scattering to the neighbourhood of the refracted and reflected beams,

(*ii*) the sudden brightening up of the opalescent spot in all azimuths when the direction of observation approaches the critical angle, and

(*iii*) the simple relation which the direction of the electric vector in the scattered light bears to that of the incident beam.

The dependence of the intensity of scattering on the surface tension and the refractive index which is clearly shown by intensity measurements for a large number of organic compounds is also indicated by the calculated values. The distribution of intensity in different azimuths has been experimentally determined. The calculated values, however, show a too rapid increase as the azimuth $\phi = O$ is approached.

(4) Critical temperature phenomena in the case of liquid carbon dioxide have been studied experimentally. As the critical temperature is approached from below, the surface scattering observed at the critical angle from below in the plane of incidence is found to increase very rapidly to a maximum value at 31·131°C. beyond which the surface gets too rough to reflect any light and developes a thick surface-layer, the scattering by which is much stronger than in the rest of the track and is visible equally well in all directions unlike genuine surface-scattering.

The liquid phase persists till the temperature rises to 31·377°C. during which interval the transition layer gets thicker and thicker and finally fills the whole bulb.

While approaching the critical temperature from a higher temperature, the liquid phase does not re-appear at 31·377°C. Even below this temperature the single phase persists till 31·131°C. at which temperature the medium gets very cloudy and translucent and slowly separates into two clear layers. The presence of only a single phase above 31·131°C. for '*falling temperature*' is probably due to the two phases observed with '*rising temperature*' in the same region being thoroughly mixed up into a stable emulsion. The phenomena below 31·131°C. are perfectly reversible.

(5) The intensity of the light scattered by the surface of liquid carbon dioxide has been measured for a range of a degree below 31·131°C. in which the intensity alters rapidly. The obtained values show a very rapid increase on approaching

31·131°C. and compare well with the values calculated from theory. This suggests that Gans' theory agrees better in the case of liquid surfaces near the critical temperature when the roughness is at its maximum.

The above work was carried out at the Indian Association for the Cultivation of Science and the author's best thanks are due to Prof. C. V. Raman, F.R.S., for his constant encouragement and guidance.

11. The Molecular Scattering of Light in Aqueous Solutions.

Part I

BY

S. VENKATESWARAN.

The molecular scattering of light in binary mixtures of some organic liquids has been studied by Martin and Lehrman (Journ. Phy. Chem., 1922, 26, 75), Raman and Ramanathan (Phil. Mag., 1923, [vi], 45, 213) and Rav. (Proc. Ind. Assoc. Cult. Science, 1924, 9, 19) and their results show in general a good agreement with the theory put forward by Raman and Ramanathan. Aqueous solutions of strong acids cannot, however, be considered simple mixtures in the sense contemplated in the above theory and it would be interesting to investigate how far such solutions conform to the theory for ordinary binary mixtures. With this object the light scattering in aqueous solutions of some acids has been investigated in this laboratory, and this part deals with solutions of nitric, hydrochloric and sulphuric acids. The results on weak acids will form the subject matter of the second part.

Experimental.

The acids used were all Merck's extra-pure chemicals rendered optically dust-free by repeated slow distillations in sealed double bulbs of the pattern used by previous investigators. It is well known that boric acid glasses are very resistant to water, nitric acid and sulphuric acid, while they are much less so to hydrochloric acid, than ordinary soda glass. (Dictionary Appl. Phys. Glazebrook, IV, 104). Sulphuric and nitric acids were therefore experimented in bulbs made of pyrex glass, and ordinary soda glass bulbs were used for hydrochloric acid.

The distillations were carried out in a dark room in the case of nitric acid to prevent the action of light. In all cases the acids were completely distilled off during the final distillation so that the bulbs were as dry as possible.

The experimental details were exactly the same as mentioned by Krishnan (Phil. Mag., 1925, [vi], 50, 697) in his paper on the molecular scattering of light in liquids.

The depolarisation of the transversely scattered light was measured as usual by Cornu's method. In the case of nitric and sulphuric acids, the depolarisation was measured for the different parts of the spectrum using coloured filters for the purpose. In all cases the intensities of the scattered light were compared directly with that of dust-free distilled water, with the help of an Abney rotating sector photometer.

Immediately after the depolarisation and intensity measurements were over, the bulb containing the acid was cut open and the strength of the acid determined by titrating a known volume of the acid against standard sodium hydroxide solution. From the temperature at which the acid was taken from the bulb and the known density corrections the exact strength of the acid was determined.

Results.

Table I gives the results of the measurements on the depolarisation of the transversely scattered light. For comparison the values obtained by Krishnan (*loc. cit.*) for water are also given. Table II gives the observed intensities of the scattered light in terms of the light scattered by water.

TABLE I.

The depolarisation of the transversely scattered light (at 30° C.).

Strength of acid %	$\frac{\text{Weak component}}{\text{Strong component}} \times 100$					
	White incident light	Orange filter in the path of		Blue filter in the path of		Calculated value
		incident light	scattered light	incident light	scattered light	
Nitric acid						
14·12	35·51	35·10	35·25	35·71	35·37	30·83
28·06	41·06	40·82	41·21	42·17	41·21	43·46
39·20	48·38	48·72	48·80	48·66	47·78	50·58
46·00	57·20	57·90	57·90	57·60	57·64	54·39
64·69	64·14	60·34	61·12	66·78	65·58	64·14
Hydrochloric acid						
6·20	16·20	...	...	...	...	12·08
13·48	18·66	...	...	...	...	15·61
15·31	18·75	...	...	...	...	16·40
20·44	18·80	...	...	...	...	18·80
Sulphuric acid						
20·38	11·07					12·56
46·82	15·60	15·61	14·13	21·02	16·20	18·80
64·06	25·96	23·77	24·21	33·33	26·21	22·83
80·00	33·75	30·23	29·90	40·59	33·62	26·83
95·90	32·68	28·28	29·00	39·25	35·25	30·78
100·00	31·40*					31·40
Water	9·6	8·5	11·8	14·5	9·9	9·6

* Value obtained by extrapolation.

TABLE II.

Intensity of the transversely scattered light (white incident light).

Strength of acid %	Intensity at 30°C.—relative to water = 1			
	Density scattering	Concentration scattering	Total	Observed value
Nitric acid				
14·12	2·05	...	...	2·07
28·06	2·60	...	...	2·74
39·20	3·43	...	...	3·07
46·00	4·75	...	...	4·02
64·69	6·62	...	...	5·96
Hydrochloric acid				
6·20	1·19	0·16	1·35	1·14
13·48	1·31	0·37	1·68	1·37
15·31	1·33	0·32	1·65	1·36
20·44	1·36	0·35	1·71	1·50
Sulphuric acid				
20·38	1·12	0·05	1·17	1·45
46·82	1·29	0·15	1·44	1·50
64·08	1·70	0·12	1·82	1·53
80·00	2·28	0·06	2·34	1·95
95·90	2·09	...	2·09	1·92
100·00	1·98	...	1·98	1·90*

Discussion of results.

i. ***Intensity*** : The theory of light scattering by binary liquid mixtures was originally worked out by Einstein (Ann.

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* Value obtained by extrapolation.

der Physik, 1910, 33, 1275) from thermodynamical considerations and later modified by Raman and Ramanathan (*loc. cit.*). On the basis of the electromagnetic theory Rav (*loc. cit.*) has recently obtained a formula which is identical with that of Raman and Ramanathan. The intensity of the transversely scattered light is given by the expression

$$I=(\Omega_1+\Omega_2)\ \frac{6(1+r)}{6-7r}$$

where Ω_1 and Ω_2 represent the well-known expressions for the "density scattering" and "concentration scattering" respectively,

$$\frac{6(1+r)}{6-7r}$$

being the multiplying factor applied to both to take into account the observed anisotropy of the medium (r is the ratio of the components of the scattered light).

For calculating Ω_1 and Ω_2 we require to know the isothermal compressibility β and the refractive index of the mixture, and the values of

$$\frac{d\log p_2}{dk}$$

where p_2 is the partial vapour pressure of the second component and k is the concentration.

For low concentrations of the three acids in question, β has been measured by Röntgen and Schneider (Cohen and Schut, *Piezochemie*, 135). For other concentrations β was calculated from the adiabatic compressibilities determined by Schmidt (Sitz-Ber. Wien, 1905, 114, Abt. IIa, 945). The values were plotted and smoothened.

The refractive index for the F line was taken for sulphuric acid, and for want of data for the F line that for the D line was taken in the case of the other two acids. The refractive indices were reduced to the temperature of the experiment, namely 30°C., by using the Lorentz-Mossotti formula and the known coefficients of thermal expansion.

The values of

were found by the usual graphical method. In the case of hydrochloric acid the vapour tensions of HCl at 30°C. for different concentrations are available from Landolt-Bornstein Tables. In this case the acid was therefore taken as the second component. In the case of sulphuric acid, Sorel's values (Landolt-Bornstein Tables p. 1395) for the vapour pressure of water over H_2SO_4 at 30°C. were taken and water was therefore considered as the second component. No partial vapour pressure data are available for nitric acid. The total vapour pressures of nitric acid at different concentrations and temperatures have been determined by Creighton and Githens (Jour. Frankl. Inst. 1915, 179, 167). But theoretical formulae such as Porter's (Trans. Farad. Soc., 1920, XVI, 336) which may be used for approximately calculating the partial vapour pressure of one of the components from the total vapour pressure of binary organic liquid mixtures, do not seem to hold good for the acids investigated in this paper. In the case of nitric acid the concentration scattering could not therefore be calculated. From a comparison of the concentration scattering in the case of hydrochloric and nitric acids, it may however be safely assumed that this is small in magnitude compared with the density scattering.

Columns 2, 3, &4 in Table II give the density scattering, concentration scattering and the total scattering respectively. It is seen that the contribution from the concentration scattering to the total intensity of the scattered light is very small as compared with the same in binary mixtures of organic liquids studied by Rav (*loc. cit.*). This shows that aqueous solutions of these acids behave more like single substances than like binary mixtures. This view is further supported by the fact that if the concentration scattering be wholly omitted the agreement between the observed and calculated values of the intensities is actually improved. This is probably what we should expect from the well-known fact that these acids in solution form definite hydrates.

ii. Depolarisation: In the case of nitric acid there is not much difference between the values of r obtained by using differently coloured filters, whereas the difference is appreciable in the case of sulphuric acid, pointing to the existence of a feeble fluorescence of the kind observed by some previous workers in the case of certain pure liquids.

The theoretical expression for r is

$$r=\frac{6\,\Omega_3}{\Omega_1+\Omega_2+7\Omega_3}$$

where Ω_1 and Ω_2 have the same significance as before and Ω_3 determines the part of the scattering arising from the anisotropy and random orientations of the molecules. The values of Ω_3 in the case of a binary mixture of any given composition can be calculated if we know the values of r for any two other concentrations (assuming that the effective anisotropy of the molecules remains constant). The values of r given in column 7 of Table I were so calculated from the observed values for water and the strongest acid. The fair agreement between the observed and calculated values of r for nitric and sulphuric acids shows that our assumption regarding the constancy of the anisotropy of the molecules is approximately correct. The results for hydrochloric acid are however distinctly anomalous.

The intensity and depolarisation of the light scattered by sulphuric acid reach a maximum value at about 80 to 90 per cent. concentration, the values again falling down for higher concentrations. In this connection it may be pointed out that similar changes with regard to density and refractive index occur in the case of this acid.

iii. The optical anisotropy of NO'_3 and SO''_4 ions:—On an examination of Table I it is seen that the values of *r* for aqueous solutions of nitric acid are very large compared with those of sulphuric acid, even though the latter has a much higher boiling point and might therefore be expected to show a higher depolarisation. This interesting fact is in conformity with the recent observations of W. L. Bragg (Proc. Roy. Soc., 1924, A 106, 346) on the relative birefringence of crystalline nitrates and sulphates.

Let us assume with Bragg that the anisotropy of the NO'_3 and SO''_4 ions is due to the mutual electrostatic interaction of the doublets induced in the different atoms, an idea which has recently been used by Ramanathan (Proc. Roy. Soc., 1925, A 107, 684) to calculate the anisotropies of a number of simple molecules. In the case of NO'_3 it is the three oxygen atoms which would contribute in a large measure to the refractivity of the ion and they may reasonably be assumed to lie at the corners of an equilateral triangle. Owing to the mutual influence of the doublets, the polarisability of the ion for an electric vector incident in the plane of the triangle would be greater than if there had been no mutual influence, while for an electric vector incident perpendicular to the plane the polarisation would be less. This explains the large anisotropy of the ion. Taking the relative distances of the three oxygen atoms in NO'_3 to be the same as in the case of crystalline nitrates (1·89 A. U.) actual calculation on the lines of Bragg gives, for the ratio of the polarisabilities of the NO'_3 ion parallel and perpendicular to the plane of the three oxygen atoms, the value 1·66. Unfortunately we have no data for the depolarisation of the light scattered by nitric acid vapour for comparison. Extending the same ideas to SO''_4 ion where presumably the four oxygen atoms are at the corners of a tetrahedron, the ion would be more or less isotropic. This explains the much larger depolarisation values shown by aqueous solutions of nitric acid than by those of sulphuric acid.

Summary and Conclusion.

1. The paper gives the results of the investigations on the scattering of light by aqueous solutions of nitric, hydrochloric and sulphuric acids.

2. The optical anisotropy of the nitric acid molecule is found to be much greater than that of the sulphuric acid molecule. This is in consonance with the difference in the birefringence of crystalline nitrates and sulphates observed by Bragg.

3. So far as light scattering is concerned these solutions behave more like single liquids than like binary mixtures.

In conclusion the author desires to express his best thanks to Prof. C. V. Raman, F.R.S., under whose inspiring guidance the work was carried out and to his friend Mr. K. S. Krishnan for his constant help.

12. Magnetic Double-Refraction in Paramagnetic Gases.

BY

K. S. KRISHNAN.

1. *Introduction.*

The theory of spatial quantization of electron-orbits in a magnetic field was put forward independently by Sommerfeld and Debye in 1916 as a necessary basis for the quantum treatment of the Zeeman-effect. In contradistinction to the classical theory of paramagnetism, in which all orientations of the electron-orbits responsible for the permanent magnetic moments of atoms or molecules are equally probable in an external magnetic field, in the limit when the field is vanishingly small, the theory of spatial quantization assumes that only certain discrete orientations are possible. The theory may now be taken to be fairly well established directly in the case of *atomic* magnetic carriers by the recent experiments of Stern and Gerlach on the deviation of a stream of atoms in a non-homogeneous magnetic field; and indirectly in the case of *molecular* magnetic carriers by the work of Pauli, Sommerfeld and others on the calculation of the magnitude of the elementary magnetic moments from measurements of paramagnetic susceptibility.

Recently attempts have been made to get some evidence of such orientations by independent optical methods. For instance Schütz,[1] Fraser[2] and others have looked for double-refraction in a strong magnetic field, in the vapours of sodium and potassium and in oxygen, which are all paramagnetic. Schütz used fields up to 15,000 gauss, and even though his optical arrangement was capable of detecting a difference between the two principal refractive indices equal to 6×10^{-9} in the case of sodium and potassium vapours, and a difference equal to 3×10^{-10} in the case of oxygen, there was no evidence of any double refraction. The vapours of sodium and potassium have one Bohr magneton per atom,[3] and according to the rules of spatial quantization, will set themselves with their magnetic moments either along or against the direction of the incident field, the probability of their taking up the one or the other position being determined by Boltzmann's theorem. If we assume along with Langevin and others that the elementary magnetic moments are rigidly fixed to the carriers, knowing the optical anisotropy of the atoms, we can easily calculate the magnitude of the magnetic double-refraction to be expected. But we have no data for determining the optical anisotropy of either sodium or potassium. In the case of oxygen we have the necessary data for calculating the double refraction, but nitric oxide with one Bohr magneton per molecule (oxygen has two), being much simpler, we shall give the calculations for this case.

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[1] W. Schütz, quoted by W. Gerlach, Phys. Zeits. 26, 820, 1925.

[2] R. Fraser, Phil. Mag. 1, 885, 1926.

2. *Double-Refraction of Nitric Oxide in a Magnetic Field.*

If we accept Bragg's[4] ideas regarding the optical anisotropy of molecules as arising from the mutual interaction of the electric doublets induced in the different atoms by the electric field of the incident light-waves, NO-molecule being diatomic, should be optically symmetrical with respect to the line joining the N- and O-nuclei, the refractivity of the molecule for light-vibrations along the optic axis being greater than for vibrations in perpendicular directions.

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[3] J. B, Taylor, Phys. Rev. 28, 576, 1926.

[4] W. L. Bragg, Proc. Roy. Soc. A., 105, 370, 1924; see also K. R. Ramanathan, same Proceedings, 107, 684, 1925.

Let A, B $(A > B)$ be the moments induced in a molecule of NO per unit electric force in the incident light-wave, acting respectively along and perpendicular to its optic axis. Also let α be the angle which the permanent magnetic moment of the molecule makes with the same axis. Then in a magnetic field, if we neglect the diamagnetic polarisation of the molecule, the refractivity of the medium for light-vibrations parallel and perpendicular to the magnetic field are given by the relations

$$\left.\begin{aligned} n_{\parallel}-1&=2\pi\nu[A\cos^2\alpha+B\sin^2\alpha] \\ n_{\perp}-1&=2\pi\nu\left[A\frac{\sin^2\alpha}{2}+B\left(1-\frac{\sin^2\alpha}{2}\right)\right] \end{aligned}\right\} \quad \ldots \quad (1)$$

where ν is the number of molecules per c. c. of the medium in the magnetic field, which may be taken to be the same as the number outside the field since the change of volume due to magnetostriction is quite negligible. (For NO, in a field of 15,000 gauss, $\frac{\delta\nu}{\nu}$ is about 7×10^{-6} at room temperature.)

The refractivity of the medium outside the field is given by

$$n-1=2\pi\nu\frac{A+2B}{3}. \quad \ldots \quad (2)$$

Now from the theory of light-scattering by anisotropic molecules the ratio $\frac{A}{B}$ can be evaluated with the help of the formula

$$\frac{A-B}{A+2B}=\sqrt{\frac{5r}{6-7r}}, \quad \ldots \quad (3($$

where r is the ratio of the intensity of the components of the imperfectly polarised light scattered transversely by the medium, when the incident light is unpolarised.

For NO, from the measurements of Cabannes and Granier,[5] $r = 0{\cdot}026$, which gives

$$\frac{A}{B} = 1{\cdot}53.$$

Taking the refractivity at 25°C. and 1 atm. pressure

$$n - 1 = 2{\cdot}69 \times 10^{-4},$$

we get

$$2\pi\nu A = 3{\cdot}50 \times 10^{-4}$$

and

$$2\pi\nu B = 2{\cdot}29 \times 10^{-4}.$$

Substituting in (1) we obtain

$$\left.\begin{aligned} n_{\parallel} - 1 &= 3{\cdot}50 \times 10^{-4} \cos^2\alpha + 2{\cdot}29 \times 10^{-4} \sin^2\alpha \\ n_{\perp} - 1 &= 2{\cdot}29 \times 10^{-4} + 0{\cdot}60 \times 10^{-4} \sin^2\alpha \end{aligned}\right\} \tag{4}$$

Case I. $\alpha = 0$, *i.e.*, the permanent magnetic moment is along the line joining the N- and O- nuclei.

$$n_{\parallel} - 1 = 3{\cdot}50 \times 10^{-4}$$

$$n_{\perp} - 1 = 2{\cdot}29 \times 10^{-4}.$$

Hence when a magnetic field is put on, light vibrations parallel to the field are retarded by about 1·4λ for each cm. lengh of track across the magnetic field, while the perpendicular vibrations are accelerated by about 0·7λ per cm.

Case II. $\alpha = \frac{\pi}{2}$ *i.e.*, the magnetic moment is perpendicular to the optic axis.

In this case

$$n_{\parallel} - 1 = 2{\cdot}29 \times 10^{-4}$$

$$n_{\perp} - 1 = 2{\cdot}90 \times 10^{-4}.$$

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[5] J. Cabannes and J. Granier, Journ. de Physique Series VI, 4, 429, 1923.

so that parallel vibrations are accelerated by 0·7λ per cm. of path, while the perpendicular vibrations are retarded by about 0·4λ per cm.

Thus for either of the positions assumed above for the direction of the magnetic moment of the molecule, which seem to be the only probable ones, the change of refractive index due to the magnetic field is sufficiently large to be detected by ordinary interference methods.

But an actual interference arrangement in which one of the interfering beams traversed a length of over 8 cms. of nitric oxide across a magnetic field of about 10,000 gauss, gave entirely negative results, in conformity with the observations on the paramagnetic substances already mentioned. Various pressures from 1 atm. down to a few mm. of mercury were tried.

In connection with this negative result it must be pointed out that for the value of α satisfying the condition

$$\cos^2\alpha=\tfrac{1}{3}\ (i.e.,\ \alpha=54°44'),\ n_{\parallel}=n_{\perp}=n\,;$$

i.e., the difference between the principal refractive indices in a magnetic field and the mean refractive index outside the field vanishes, the difference being numerically small for values of α not far different from this value. For these directions of the permanent moment, we should therefore expect no detectable change in refractive index in a magnetic field. These directions, however, seem to be highly improbable.

3. *Magnetic Double-Refraction of Oxygen according to the Classical Theory.*

The negative result is not peculiar to the quantum theory. Even if we assume, as in the classical theory of paramagnetism of Langevin, that all orientations of the elementary magnetic moments are equally probable in a magnetic field, of course in the limit when the field vanishes, we still get a value for the double-refraction of oxygen, for instance, which could not have escaped detection in Schütz's experiments in case it exists.

As in the case of NO it is reasonable to assume that O_2-molecule has an axis of optical symmetry, *viz.*, the line joining the two O-nuclei. If as before, α denotes the angle which the permanent magnetic moment μ of the molecule makes with the optic axis, we have according to the classical theory[6],

$$n_{\parallel} - n_{\perp} = \frac{(n^2-1)(n^2+2)}{4n} \cdot \frac{\theta_1+\theta_2}{\gamma} \cdot H^2, \qquad \ldots \quad (5)$$

where

$$\theta_1 = \frac{1}{45kT} \cdot (A-B)(2A'-B'-C')$$

and

$$\theta_2 = \frac{\mu^2}{45k^2T^2}(A-B)(2\cos^2\alpha-\sin^2\alpha)$$

$$\gamma = \frac{A+2B}{3},$$

A, B have the same significance as before. A′, B′, C′ are the diamagnetic moments induced in a molecule of oxygen per unit magnetic field incident along, and in two mutually perpendicular directions at right angles to its optic axis. H is the incident magnetic field, and k is Boltzmann's constant.

A little calculation shows that for oxygen, θ_1 which depends on the diamagnetic anisotropy of the molecule, is entirely negligible in comparison with θ_2. If we take the diamagnetic values for oxygen calculated by Pascal from its compounds, even assuming that the molecule (O_2) is polarisable diamagnetically only along its optic axis, θ_1 is only about $\frac{1}{400}$ of θ_2 (numerically) when $\alpha=0$, and about $\frac{1}{200}$

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[6] See P. Debye, Handbuch der Radiology Band VI, p. 769.

of θ_2 when $\alpha=\frac{\pi}{2}$, which as in the case of NO, seem to be the only probable values for α.

Since n is very nearly equal to 1,

$$n_{\parallel}-n_{\perp}=\frac{n-1}{10k^2T^2}\cdot\mu^2\cdot H^2\,\frac{A-B}{A+2B}(2\cos^2\alpha-\sin^2\alpha)$$

$$=\frac{n-1}{10k^2T^2}\cdot\mu^2\cdot H^2\sqrt{\frac{5r}{6-7r}}\cdot(2\cos^2\alpha-\sin^2\alpha)\ \ldots\quad(6)$$

From the susceptibility measurements of Bauer and Piccard[7]

$$\left(\chi=\frac{0\cdot03158}{T}\right)$$

μ on calculation, still according to the classical theory, comes out to be equal to $2{\cdot}62\times10^{-20}$.

At 1 atm. pressure and 20°C., which may be taken as the temperature of Schütz's experiment,

$$n-1=2\cdot53\times10^{-4}.$$

Also

$$r=0\cdot0645\ \text{(Cabannes and Granier)}.$$

$$\therefore\quad n_{\parallel}-n_{\perp}=2\cdot60\times10^{-18}H^2(2\cos^2\alpha-\sin^2\alpha).$$

For

$$H=15{,}000\ \text{gauss}$$

$$n_{\parallel}-n_{\perp}=6\times10^{-10}(2\cos^2\alpha-\sin^2\alpha).\quad\ldots\quad(7)$$

When $\alpha=0$,

$$n_{\parallel}-n_{\perp}=12\times10^{-10}$$

and is hence four times the amount which Schütz could have detected, and when $\alpha=\pi/2$,

$$n_{\parallel}-n_{\perp}=-6\times10^{-10}$$

which is about twice the amount.

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[7] E. Bauer and Piccard, Journ. de Physique Series VI, 1, 97, 1920.

Thus even calculating according to the classical theory, there is no evidence of orientation of paramagnetic molecules in a magnetic field.

The same conclusions have been drawn by Debye and Huber[6] from the negative results of some experiments on nitric oxide and other substances. The molecules of NO, in addition to possessing a permanent magnetic moment, also have a small electric moment. When placed in a magnetic field, if the molecules orientate, owing to their electrical polarity they will induce a difference of potential between two parallel plates placed transversely to the magnetic field. But in their actual experiment there was no such potential difference. It might however be pointed out here that if the electric moment of the molecule is perpendicular to the magnetic moment, which is not improbable, even if there is orientation of the molecules when the field is put on, they will not induce any difference of potential.

4. *Discussion of the Results.*

A natural explanation which would suggest itself for the negative results mentioned in the previous sections, is that if paramagnetic molecules do not orientate as a whole in a magnetic field, the electron-orbits responsible for the moments of the molecules might be free to rotate without disturbing the rest of the molecule. In the case of sodium and potassium, where according to the generally accepted ideas, the single electron in the outermost orbit accounts for the paramagnetism, there is not much difficulty in considering it to be free to rotate independently of the rest of the atom. But the explanation is not without difficulties in the case of NO, for instance. The idea is not new and has been put forward to explain the observed validity of Curie's law in the case of paramagnetic crystals.

P. Debye, Zeits. f. Phys. 36, 300, 1926; A. Huber, Phys. Zeits. 27, 619, 1926.

However the above assumption is not by itself sufficient to account for the absence of any double-refraction in a magnetic field. We will have further to assume that the contributions from these paramagnetic electron-orbits to the optical anisotropy of the molecule is quite negligible. Thus, for instance, in the case of sodium and potassium we will have to assume that the difference in the deformability of the outer electron-orbit due to the electric field of the incident light-waves, when the field is acting in the plane of the orbit and when it is acting perpendicular to the plane, is very small. But when we remember that even the inert gases like argon, krypton and xenon, with closed and symmetrical configurations exhibit an appreciable optical anisotropy, as evidenced by the imperfect nature of the polarisation of the light transversely scattered by them[9], it is rather difficult to understand how the outermost electron-orbit in sodium or potassium can be so perfectly isotropic.

5. *Summary.*

According to the theory of spatial quantization, which may be taken to be fairly well established, the molecular magnetic moments in nitric oxide, equal to one Bohr-magneton each, should all orientate in a magnetic field with their axes either along or against the field. If the moments are rigidly fixed to the molecules, the latter being optically anisotropic, the medium should exhibit a double refraction as a consequence of the orientation.

The magnitude of the double refraction to be expected is calculated. But actually no such double-refraction could be detected.

The negative result is then shown to be not peculiar to the quantum theory. In the case of oxygen, for instance, Schütz could not discover any double-refraction in a strong magnetic field, while calculation accordng to the classical theory shows that the effect could not have escaped detection in Schütz's experiment in case it exists.

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[9] See J. Cabannes and A. Lepape, Comptes Rendus 179, 325, 1924.

It is therefore evident that paramagnetic molecules do not orientate, at least as a whole, in a magnetic field.

Some difficulties in the different explanations that might be suggested for these negative results, are pointed out.

In conclusion the author wishes to express his best thanks to Prof. C. V. Raman for his kind interest in the work.

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The 6th December, 1926.

13

A Relation between the Specific Heat, Thermal Expansion, and Velocity of Sound in Liquids

BY

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1. *Introduction.*

Some years ago, in a paper[1] bearing the title of " Isentropic coefficient of expansion," Mr. Satyendra Ray pointed out that the quantity

$$\sqrt{C_p/a_p}$$

(where C_p=the specific heat and a_p=the coefficient of volume expansion), which has the dimensions of a velocity, is for all states of matter—solid, liquid and gaseous—a quantity of the same order of magnitude as the velocity of sound in the substance concerned. The ratio of these two quantities, he points out, is roughly equal to unity for liquids. Mr. Ray, in his paper, gives the data for five liquids only[1] and proceeds to a discussion based essentially on the assumed equality of the two quantities under consideration.

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[1] Satyendra Ray, Phy. Rev., Vol 15, p. 24 (1920).

It appeared worth while to base a discussion on more extensive data and to examine the relation between the two quantities in question, and their alleged equality in a more critical manner. It seemed also that it might be profitable to consider the interpretation of this undoubtedly interesting relationship from the standpoint of molecular theory.

2 *Discussion of the Data.*

The following table shows the results of calculating the values of $\sqrt{C_p/\alpha_p}$ and $\sqrt{E_\phi/\rho}$ for a number of liquids. They have been calculated for some convenient temperature for each case, and the appropriate values of C_p, α_p, E_ϕ and ρ for the particular temperature have been taken so as to avoid errors creeping in on account of the temperature variations of these quantities. The adiabatic elasticity E_ϕ was calculated from a knowledge of the isothermal compressibility β from the tables, and with the help of the formula

$$\beta = \alpha' + \frac{T\alpha_p^2 v}{J.C_p}$$

where α' = the adiabatic compressibility (*i.e.*, $\frac{1}{E_\phi}$), v = the sp. volume, T the absolute temperature and J the mechanical equivalent of heat. Values of β were chosen as much in the neighbourhood of normal pressure as possible.

Mr. Ray's figure for $\sqrt{C_p/\alpha_p}$ in the case of water seems to be an error.

Table I.

Substance	Temp.	$\sqrt{E_\phi/\rho}$ in metres per sec.	$\sqrt{C_p/\alpha_p}$ in metres per sec.	Ratio $\frac{\sqrt{E_\phi/\rho}}{\sqrt{C_p/\alpha_p}}$
Aniline ...	25°c	1736	1550	1·12
Acetic acid ...	0°c	1793	1568	1·14
Benzene ..	70°c	1099	1165	0·94
	0°c	1402	1190	1·18
Chloroform ...	0°c	1055	887	1·19
Bromine ...	20°c	899	652	1·38
Chlorobenzene ...	20°c	1275	1166	1·10
Carbonbisulphide	0°c	1210	932	1·3
Carbon tetrachloride	0°c	988	842	1·17
Ether ...	0°c	1089	1219	0·83
Ethyl acetate ...	13°c	1225	1208	1·014
Ethyl alcohol ...	0°c	1219	1490	0·82
Ethyl chloride ...	15°c	1040	1026	1·01
Ethyl bromide ...	99°c	543	807	0·7
Glycerine ...	20°·5c	1894	2144	0·88
Methyl alcohol ...	14°·7c	1240	1433	0·87
n-Propyl alcohol ...	17°·7c	1227	1624	0·76
iso-Propyl alcohol	17°·7c	1258	1519	0·83
Olive oil ...	20°·5c	1411	1679	0·83
Turpentine ...	8°·5c	1371	1440	0·94
Mercury ...	20°c	1462	873	1·7
Pentane ...	20°c	947	1182	0·8
Water ...	100°c	1559	2371	0·66
Toluene ...	0°c	1389	1212	1·14

Variation with temperature

Table II gives the variations of

$$\sqrt{C_p/a_p} \text{ and } \sqrt{E_\phi/\rho}$$

with temperature for some selected liquids. The data required for these calculations were taken from a paper by Daniel Tyrer.[1]

TABLE II unit=metre/sec

	Substance.		0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100°C
1	**Chlorobenzene**	$\sqrt{C_p/a_p}$	...	...	1166	1174	1181	1190	1198	1196	1193	...	...
		$\sqrt{E_\phi/\rho}$	...	...	1275	1240	1206	1172	1140	1108	1076	...	...
2	**Chloroform**	$\sqrt{C_p/a_p}$	887	885	879	872	864	856	847	...	...	...	...
		$\sqrt{E_\phi/\rho}$	1055	1023	992	962	932	902	876	...	...	...	...
3	**Ether**	$\sqrt{C_p/a_p}$	1219	1211	1203	1189	...	...	...	...	...	...	...
		$\sqrt{E_\phi/\rho}$	1089	1040	997	956	...	...	...	...	...	...	...

4	**Benzene**	$\sqrt{C_p/a_p}$	1190	1191	1190	1188	1187	1182	1179	1165	...	...	...
		$\sqrt{E_\phi/\rho}$	1402	1354	1310	1268	1225	1181	1140	1099	...	...	...
5	**Toluene**	$\sqrt{C_p/a_p}$	1212	1229	1247	1266	1278	1286	1276	1271	...	...	...
		$\sqrt{E_\phi/\rho}$	1389	1349	1309	1272	1236	1198	1156	1116	...	...	...
6	**Carbon bisulphide**	$\sqrt{C_p/a_p}$	932	928	918	907	891	875	...	...	...	...	...
		$\sqrt{E_\phi/\rho}$	1210	1181	1149	1120	1087	1054	...	...	...	...	...
7	**Ethyl alcohol**	$\sqrt{C_p/a_p}$	1490	1505	1520	1533	1545	1549	1551	1555	1559	...	...
		$\sqrt{E_\phi/\rho}$	1219	1180	1151	1120	1090	1059	1029	996	971	...	...
8	**Carbon tetrachloride**	$\sqrt{C_p/a_p}$	842	840	838	833	823	813	801	788	776	...	...
		$\sqrt{E_\phi/\rho}$	988	959	931	920	874	845	817	790	763	...	...
9	**Water**	$\sqrt{C_p/a_p}$	...	6915	4505	3785	3332	3053	2845	2695	2569	2461	2371
		$\sqrt{E_\phi/\rho}$	...	1447	1482	1509	1526	1538	1545	1552	1555	1558	1559

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[1] D. Tyrer: J. C. S. Trans. CIII. Part II. p. 1675-88 (1913).

It is obvious from the above that the ratio

$$\sqrt{E_\phi/\rho}\Big/\sqrt{C_p/a_p}$$

is different for different liquids and different for the same liquid at different temperatures. In some cases, however, there is a remarkably close agreement between them but this does not warrant our taking their ratio to be unity universally, seeing, as we do, that it is in most cases far from it.

For all liquids in table II except water, we see that $\sqrt{E_\phi/\rho}$ regularly diminishes as the temperature rises, while for water it is the reverse.

$\sqrt{C_p/a_p}$ shows a regular increase in the case of ethyl alcohol. With toluene, benzene and chlorobenzene, it first rises and then falls. As remarked in a footnote, Mr. Ray's value for $\sqrt{C_p/a_p}$ in the case of water is an error. Even at 100°C. there is no agreement between the two quantities under discussion.

The relation between them therefore, must depend ultimately upon the molecular structure of the liquid and must therefore be looked for in molecular theory.

3. *Interpretation by Molecular Theory.*

I have attempted to derive such a relation from van der Waals' Equation of state, *viz.*,

$$p+\frac{a}{v^2}=\frac{RT}{v-b} \qquad (1)$$

We shall throughout consider 1gm. mol. of liquid. The total energy of the molecules $=mE$, m being the mol. wt. in gms. and E the total energy / unit mass. The translatory energy of the molecules $=\frac{3}{2}$ RT.

∴ If λ be the ratio of the *total* to the *translatory* energy, we have

$$mE=\frac{3}{2}\lambda RT.$$

Substituting from this in (1) we have

$$p+\frac{a}{v^2}=\frac{2}{3}\,\frac{m\mathrm{E}}{\lambda}.\frac{1}{v-b}$$

$$=\frac{2}{3}\,\frac{\rho v\mathrm{E}}{\lambda}.\frac{1}{v-b}.$$

$$\therefore\quad\left(\frac{dp}{dt}\right)_v=\frac{2\rho}{3\lambda\left(1-\frac{b}{v}\right)}\cdot\left(\frac{d\mathrm{E}}{d\mathrm{T}}\right)_v \qquad \ldots \quad (2)$$

But

$$\left(\frac{dp}{dt}\right)_v=\left(\frac{dp}{dv}\right)_t\cdot\left(\frac{dv}{dt}\right)_p=\frac{\mathrm{E}_\theta}{v}\times v a_p=\frac{\mathrm{C}_v}{\mathrm{C}_p}\cdot\mathrm{E}_\phi : a_p$$

since

$$\frac{\mathrm{E}_\theta}{\mathrm{E}_\phi}=\frac{\mathrm{C}_v}{\mathrm{C}_p}.$$

We know also

$$\left(\frac{d\mathrm{E}}{d\mathrm{T}}\right)_v=\mathrm{C}_v$$

∴ (2) becomes, after substitution,

$$\frac{\mathrm{C}_v}{\mathrm{C}_p}\,\mathrm{E}_\phi\cdot a_p=\frac{2\rho\mathrm{C}_v}{3\lambda\left(1-\frac{b}{v}\right)}$$

or

$$\sqrt{\mathrm{E}_\phi}/\rho=\sqrt{\mathrm{C}_p/a_p}\quad\sqrt{\frac{2}{3\lambda\left(1-\frac{b}{v}\right)}} \qquad \ldots \quad (3)$$

van Laar's Equation of state

But van Laar has shown[1] that van der Waals' equation which assumes constant values for '*a*' and '*b*' is not valid, specially for liquids and solids, and has derived the more correct equation

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[1] van Laar: Proc. Royal. Acad. Amsterdam, Vol. 27, p. 897-913 (1924).
van Laar: Zustandsgleichung von Gasen und Flussigkeiten. Leipsig-Ed., 1924.

$$p+\frac{a}{v^2}=\frac{\gamma_s}{v}L \qquad \ldots \quad (4)$$

where L = progressive energy of the molecules

$$\gamma_s=\frac{\frac{2}{3}\left(1+\frac{2b_o}{v}\right)}{1-\frac{b_o}{v}},$$

b_o=value of b when $v=v_o$ *i.e.*, at abs. zero

As before we have $\lambda L=mE$

$$\because \; p+\frac{a}{v^2}=\frac{\gamma_s mE}{v\lambda}=\frac{\gamma_s \rho E}{\lambda}$$

$$\therefore \; \left(\frac{dp}{dt}\right)_v=\frac{C_v}{C_p}\cdot E\phi\cdot a_p=\frac{\gamma_s\rho C_v}{\lambda}$$

i e.,

$$\sqrt{E\phi/\rho}=\sqrt{C_p/a_p}\;\sqrt{\frac{2}{3}\left(1+\frac{2b_o}{v}\right)\Big/\left(1-\frac{b_o}{v}\right)\lambda} \qquad \ldots \quad (5)$$

Equation (5) gives us then a ratio between the two quantities concerned, which differs from what we got from van der Waals' Equation in that it has an additional term

$$\sqrt{1+\frac{2b_o}{v}}$$

in the numerator, thus increasing the value of the ratio. Again, we have here to deal with the quantity b_o instead of b.

Verification of the relation.

The quantity

$$\sqrt{\frac{\frac{2}{3}\left(1+\frac{2b_0}{v}\right)}{\left(1-\frac{b_0}{v}\right)\lambda}}$$

should then be calculated to see if the ratio calculated from this formula fits in with the results of tables I and II. For some liquids, calculated values of b_0 and v were available from van Laar's "Zustandsgleichung von Gasen und Flussigkeiten" and for others they were calculated from other data available from the same book, *viz.*, that

$$b_0 = v_0; \quad \frac{b_0}{v} = \frac{v_0}{v} = \frac{D}{D_0}$$

if D=density

$$D_0 = 2D_k \left\{ 1 + \frac{1+\cdot 038\sqrt{T_k}}{2} \right\},$$

D_k, being the density at crit. temp. T_k (abs.)

and

$$\frac{b_k}{v_k} = \frac{1}{2} \; \frac{1+\cdot 038\sqrt{T_k}}{1+\left(\frac{1+\cdot 038\sqrt{T_k}}{2}\right)}.$$

Where these were not available, a very good approximation could be got by putting $v = v_0(1+\alpha T)$, neglecting higher powers of α.

$$\frac{b_0}{v} \qquad \frac{1}{1+\alpha T},$$

λ was calculated from the following considerations :

$$L = \frac{3}{2} RT \text{ , neglecting higher powers of } \frac{1}{T}$$

$$= \frac{mE}{\lambda}$$

$$\therefore \quad \frac{dE}{dT} = C_v = \frac{3}{2} R'\lambda,$$

$R' =$ Gas const. / gm.

$$\therefore \lambda = \frac{2}{3} \frac{C_v}{R'}$$

Knowing C_v and R', λ was calculated. Where C_v was not known directly, it was calculated from the well-known relation

$$\frac{C_v}{C_p} = \frac{E_\theta}{E_\phi} .$$

Table III gives the values of the ratio

$$\sqrt{E_\phi / \rho} \Big/ \sqrt{C_p / a_p}$$

calculated from (5) in comparison with those given by Tables I and II.

TABLE III.

Substance.	Temp.	Ratio from (5).	Ratio from I and II.
Ethyl chloride ...	15°C	1·005	1·01
Carbon bisulphide ...	0°C	1·35	1·3
Carbon tetrachloride ...	0°C	0·99	1·17
Ether ...	20°C	0·74	0·83
Chloroform ...	0°C	1·03	1·19
Glycerine ...	20·5°C	0·91	0·88
Pentane ...	20°C	0·75	0·84
Benzene ...	0°C	0·99	1·18
	70°C	0·87	0·90
Bromine ...	20°C	1·402	1·38
Ethyl alcohol ...	0°C	0·9	0·82
Ethyl bromide ...	99°C	0·8	0·7
n-Propyl alcohol ...	17·7°C	0·86	0·76
iso-Propyl alcohol ...	17·7°C	0·84	0·83

The table shows a good agreement between the two values of the ratio. The divergence in some cases is probably due to the approximation involved in the calculation.

If $\sqrt{C_p/a_p}$ and $\sqrt{E\phi/\rho}$ were exactly equal to each other, then we should find, on equating their ratio to 1, that

$$\lambda + \frac{4}{3} = \frac{2v}{v - b_e} \,.$$

From this approximate equality then, we can interpret the relation (5) as indicating an intimate relationship between the ratio of the *total* to the *translatory* energy of the molecules and the ratio of the *total* to the *free* volume of the liquid.

4. *Summary and Conclusion.*

Mr. Satyendra Ray's observation in the Physical Review for January, 1920 that

$$\sqrt{C_p/a_p} = \sqrt{E\phi/\rho}$$

for liquids is examined with more extensive data and the relation is tested at varying temperatures. An approximate and not exact equality is found, even after correcting for the variations of the quantities involved.

An interpretation on molecular theory is attempted, and relations connecting the quantities derived from van der Waals' and the more applicable van Laar's equations of state. The relation

$$\sqrt{E\phi/\rho} = \sqrt{C_p/a_p} \quad \sqrt{\frac{\frac{2}{3}\left(1 + \frac{2b_e}{v}\right)}{\left(1 - \frac{b_e}{v}\right)\lambda}}$$

is found from the latter and, on actual calculation in a number of cases, is found to give the same ratio as is got from calculations of $\sqrt{E\phi/\rho}$ and $\sqrt{C_p/a_p}$.

There is an intimate relationship between the ratio of the *total* to the *translatory* energy of the molecules and the ratio of the *total* to the *free* volume of the liquid.

In conclusion, the author expresses his respectful thanks to Prof. C. V. Raman, F. R. S., for his suggestions, guidance and help.

CALCUTTA :
12-12-1926.

On a New Method of Comparing Viscosities of Liquids by Oscillating Columns.

BY

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1. *Statement of the Problem.*

The following problem deals with the *free* oscillations of liquids (which wet glass) contained in U-tubes provided with 'easy' bends, *i.e.*, free from angular or sharp bends and from deformations of the bore. The primary object of the investigation is to study the effect of viscosity on the damping of such oscillations.

From the experimental data it will be seen that the bore of the widest tube used on the present occasion is a little less than one cm. in diameter and as the amplitude in most of the cases hardly exceeds two mms. the instantaneous velocity of the column of liquid is far short of the 'critical' value, as can be seen from Reynolds number;[1] for instance, when the diameter is one inch the limiting value is reached for a velocity of about 2 ft. per sec. In what follows, therefore, the motion of the liquid is assumed to be what Reynolds calls 'direct', *i.e.*, parallel to the sides of the tube and not sinuous.

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[1] The Philosophical Transactions of the Royal Society—1883. (col. works, Vol. II, pp. 50-105).

2. *Mathematical Theory.*

From the well-known sets of equations[1] for the steady flow of a viscous liquid through a cylindrical tube we have:

$$w = K(a^2 - r^2) + U \qquad \ldots \quad (1)$$

where w is the velocity parallel to the axis of the tube, K a constant and 'a' the radius of the tube. w shall have a finite value w_o when $r=o$, *i.e.*, along the axis of the tube and $w=U$ when $r=a$, *i.e.*, near the walls. Since the liquid film in immediate contact with the walls is at rest the liquid slips past this film with a velocity of U and has its maximum value w_o along the axial line. In capillary tubes and for insensibly small velocities the slipping is zero and hence $U=o$ and we have the well known Poiseuille's results.

But in the case of oscillatory motion, however. the boundary conditions are not simple nor is there an easy means of studying them. It is a matter of common observation that when the liquid column oscillates down it leaves a trail of liquid behind which continues to drain down so that when the column oscillates up the surface of separation is really the surface of contact of two liquid films having opposite velocites. This, however, lasts for a short time. Then again in oscillatory motion it can be seen that the column of liquid near the walls comes to rest sooner than that farther within.

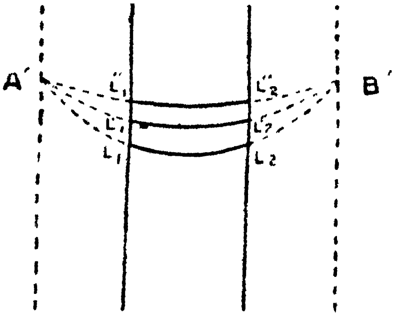

FIG. I.

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[1] Stokes, vol. I, pp. 75-129.

Consider, therefore, a cylindrical column of the liquid away from the *boundary layer* and near the axis. Let AB be an imaginary surface enclosing this liquid column and L_1L_2 the level of the liquid initially. When the column is set oscillating, the free surface takes up in succession the positions $L_1' L_2'$, $L_1'' L_2''$ ....and the curvature of the surface is changed in a way with which we are quite familiar. If the amplitude is small, as is the case in the present investigations, it may be assumed that these curves $L_1 L_2$, $L_1' L_2'$.............. when continued outside the surface AB meet at two imaginary points A′ B′ symmetrically situated with respect to AB. Imagine, therefore, that the surface AB is surrounded with a *fictitious* tube, the diameter of which is A′B′ and that the column of liquid AB forms a part of the wider column filling the tube A′B′ and oscillating in such a manner that the two ends A′ and B′ remain relatively fixed. If now the radius of the fictitious tube is ‘ *b* ’, equation (1) takes the simplified form

$$w = K(b^2 - r^2) \qquad (2)$$

and there is no slipping when $r = b$.

The value ‘ $2b$ ’ when r is ultimately made zero, may be called the *reduced diameter* of the tube. It is assumed that for a given tube and for different *wetting* liquids, it is a constant—the validity of such an assumption being borne out by the results of the present investigation.

b is, therefore, the radius of a fictitious tube the central column of which has oscillatory motion identically similar to that of the central column of the experimental tube and at the boundaries of which there is no slipping.

If s is the vertical displacement of one end of a cylindrical shell of radius r and thickness δr we have from(2)

$$s = A(b^2 - r^2) \qquad \ldots \quad (3)$$

where A is a function of time. Thus at a given instant $s=o$ when $r=b$, *i.e.*, at the walls of the fictitious tube and $s=s_o$ when $r=o$.

Before, however, the equation of motion for free oscillations is set down the effect of the atmospheric pressure and of surface tension on the free annular ends of the shell must be found.

(1) Effect of the atmospheric pressure.

If P is the atmospheric pressure, the vertical component of the pressure is:

$$P \times 2\pi r \times \delta s .\ \cos(n, v)$$

where δs is the length along the arc and $\cos(n, v)$ the cosine of the angle between the normal and the vertical.

$$= P \times 2\pi r \times \delta r \quad \text{since } \delta s \cos(n, v) = \delta r.$$

Treating similarly the other end of the shell the effect of pressure on the two free ends:

$$= P \times 2\pi r \times \delta r - P \times 2\pi r \times \delta r = 0 \quad \ldots \quad (4)$$

(2) Effect of surface tension.

Let

$$Z = A(b^2 - r^2) + A_o r^2$$

where A_o is a constant and Z is distance above the plane through the lowest point of the surface when at rest.

Resultant upward component of surface tension at one end

$$=\delta r.\frac{d}{dr}\left\{ T \times 2\pi r \cos(t,v) \right\}$$

where t, v stand for tangent and vertical respectively.

Taking the effect of surface tension at the other end also, removing common terms, dividing it by $2\pi r\delta r l m\ (b^2-r^2)$ where l is the total length of the liquid column and m the density—the reason for so dividing will be plain from equation (8) below—and putting $r=o$, we have finally for the effect of surface tension

$$\frac{8TA_o}{lmb^2} \qquad \ldots \quad (5)$$

where A_o, as will be remembered, is a constant. Hence the effect of surface tension is to add a constant factor (5) to the following equation of motion.

(3) Equation of motion.

The difference in the tangential tractions[1] on the two curved surfaces of the whole cylindrical shell of length l and of surface area $2\pi r l$ is

$$-\frac{\partial}{\partial r}\left(\mu.\ \frac{\partial w}{\partial r}\ 2\pi r l \right)\delta r \qquad (6)$$

where μ is the coefficient of viscosity.

The equation of motion of this cylindrical shell oscillating freely under its own weight is

$$2\pi r\delta r \times lm\ \frac{d^2s}{dt^2} + \frac{\partial}{\partial r}\left(\mu.\ \frac{\partial w}{\partial r}\ 2\pi r l \right)\delta r + 4\pi r\delta r s m g = 0 \qquad \ldots \quad (7)$$

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[1] Lamb, Hydrodynamics 4th edition p. 577.

the third term to the left of (7) becomes

$$2\pi r\delta r s m g\ (\mathrm{Sin}\ \theta_1+\mathrm{Sin}\ \theta_2)$$

if the arms of the bent tube are supposed to be inclined at θ_1 and θ_2 to the horizontal. To (7) must be added the constant (5). In investigating the effect of viscosity on damping the oscillations, neglect of this term is of no consequence since it affects only the centre of oscillation and leaves the period and the damping unaltered. The logarithmic decrement in such cases is calculated by noting three successive swings to the same side of zero.

Remembering (3) and simplifying, equation (7) takes the form

$$\frac{d^2A}{dt^2}+\frac{4\mu.}{m(b^2-r^2)}\cdot\frac{dA}{dt}+\frac{2g}{l}\cdot A=0 \qquad \ldots \quad (8)$$

On solving this equation we get:

$$\mu=\frac{mb^2\lambda}{2\tau\left(1+\frac{\lambda^2}{8\pi^2}\right)} \qquad \frac{mb^2\lambda}{2\tau'}$$

where λ is the log. dec. for a complete period of a point on the axis for which $r=o$, τ is the periodic time and τ' that corrected for damping.

Now that $\frac{\mu}{m}=\gamma$ the kinematic coefficient of viscosity, the above expression ultimately becomes:

$$\gamma=\frac{b^2\lambda}{2\tau\left(1+\frac{\lambda^2}{8\pi^2}\right)} \qquad \ldots \quad (9)$$

as can be verified by dimensional considerations.

Thus the coefficient is found in terms of the reduced radius b, Log. dec. λ and the periodic time τ. Since the periodic time depends only on the total length of the liquid column, the coefficients of viscosity are compared by filling the same tube with different liquids to the same height and noticing the log. decrements in each case. This is the method adopted on the present occasion.

3. *Experiment.*

The experiment is conducted with five glass tubes of diameters 0·94, 0·65, 0·60, 0·56 and 0·39 cms. respectively, of which the second (namely, of diam. 0·65cm.) has its arms inclined at about 8° to the horizontal and the rest have their arms very nearly vertical. Of these four tubes the inclination of the arms to the vertical in no case exceeded about a degree and half. The uniformity of the bore before and after each of these glass tubes is bent is tested by the usual method. The process of bending the tubes so as to satisfy these conditions is a matter of some difficulty and I thank my friend and colleague Mr. D. Gunnaiya for having kindly and willingly undertaken to do this work for me. Out of eleven tubes chosen for the experiment five were found suitable for the purpose.

Before these tubes are filled up with different liquids all possible care is taken to see that they are cleaned *thoroughly* well and rendered free from all trace of grease. Indeed the success of these experiments seemed to depend on the cleanliness of the tubes. Each of the tubes is filled up with a solution of potassium dichromate in concentrated sulphuric acid and is allowed to remain thus filled, overnight. It is then washed in plenty of running tap water and is cleaned once again with concentrated nitric acid. As the acids get diluted with use they are rejected after using them twice and fresh acids taken. Finally the tubes are washed in plenty of running tap water. They are then allowed to dry for one full day in a dust-free chamber. The dry tube is rinsed with the liquid with which it is desired to be filled up. As this process of cleaning is repeated with each tube and before it is filled up with each of the liquids, these experiments extended for over nine months.

A fine mark is made with a diamond pencil on the outside of the tube and at a distance of about 4 cms. from one end. Each tube is filled in succession with the different liquids up to this mark so that l the total length of the liquid column is the same. The two ends of the bent tube are provided with two peices of rubber tubing each about 3-4 cms. in length. A telemicroscope having a scale divided into tenths of a mm. within its eye-piece is focussed on the surface of the liquid. For purposes of observation it is found a great advantage if an electric bulb is held at a suitable distance so that a fine streak of light reflected from the meniscus of the liquid surface is seen clearly focussed. The position of the bulb is, of course, found by trial. On gently pinching and releasing the free end of either of the two rubber tubings attached to the ends, the liquid column is set oscillating and by a little practice the range of oscillations is easily controlled. In the present experiments the initial amplitude is in most cases about two mms. and in no case is it allowed to exceed 3 mms. Three successive swings to the same side of the position of equilibrium are read correct to a tenth of a division. In view of the fact that the amplitude is so small and the period of oscillation, in most cases, over one sec. a sufficiently quick and trained eye can take readings correct to a tenth of a division. In this way quite a large number of observations are made with each liquid. From considerations of space the mean of closely agreeing values are tabulated below.

4. *Results.*

Since the coefficients of viscosity of different liquids are compared with that of water the following preliminary experiment is conducted to find μ for water by the usual capillary tube method.

Temp. of water 28°·6 C. Volume of water collected 100c.c.

Time to collect 100 c.c. of water (mean of 8 determinations) = 29′16″

radius of the bore = 0·0395 cm.; length of tube = 24·5cms.

$P = 12{\cdot}65 \times {\cdot}9960 \times g$ dynes per sq. cm.

$\therefore \quad \mu = 0{\cdot}008457$ poises at 28°·6.c.

Temp. varied between 30° – 28°·5 C.

TABLE NO. I.

Liquid.	Density at 30°C.	No. 1. Diam. 0·94 cm.; l = 130·9 cm. Arms vertical and 21·5 cm. apart.		No. 2. Diam. 0·65 cm.; l = 67·3 cm. Arms inclined 8° to horizontal.		No. 3. Diam. 0·60 cm.; l = 84·8 cm. Arms vertical and 13·5 cm. apart.		No. 4. Diam. 0·56 cm.; l = 84·6 cms. Arms vertical and 18 cm. apart.		No. 5. Diam. 0·39 cm.; l = 83·9 cm. Arms verical and 16 cm. apart.	
		λ	μ	λ	μ	λ	μ	λ	μ	λ	μ
	gms. per cc										
Water ...	0·9960	0·5252	0·008457	1·098	0·008457	0·7645	0·008457	0·8626	0·008457	1·387	0·008457
Alcohol (ethyl)...	0·794	0·7544	0·009685	1·579	0·009687	1·098	0·009687	1·232	0·009647		
Ether ...	0·712	0·2922	0·003364	0·6325	0·003481	0·4289	0·003392	0·4863	0·003409	0·7968	0·003480
Benzene ..	0·873	0·4336	0·006120	0·9116	0·006152	0·6400	0·006214	0·7145	0·006141	1·142	0·006103
Xylene ...	0·871	0·4513	0·006356	0·9539	0·006422	0 6658	0·006440			1·193	0·006363
Turpentine ...	0·862	0·8401	0·01168	1·739	0·01158	1·210	0·01158				
Carbon di-Sulphide. ...	1·289	0·2213	0·004613	0·4706	0·004689	0·3295	0·004719			0·5947	0·004693

Densities in column (2) are taken from Castell-Evans 'Physical and Chemical' tables. Tube No. 4 was unfortunately broken before I could experiment with other liquids. Tube no. 5 has a very narrow bore and the damping in consequence great. With small amplitudes which the theory presupposes it is not practicable to find λ for relatively viscous liquids, namely: alcohol and turpentine.

TABLE NO II.

Radius (a)	Reduced radius (b)	b/a.
0·47 cm.	0·2296 cm	0·4885
·325 „	·2214 „	·6813
·30 „	·1710 „	·5701
·28 „	·1611 „	·5753
·195 „	·1277 „	·6549

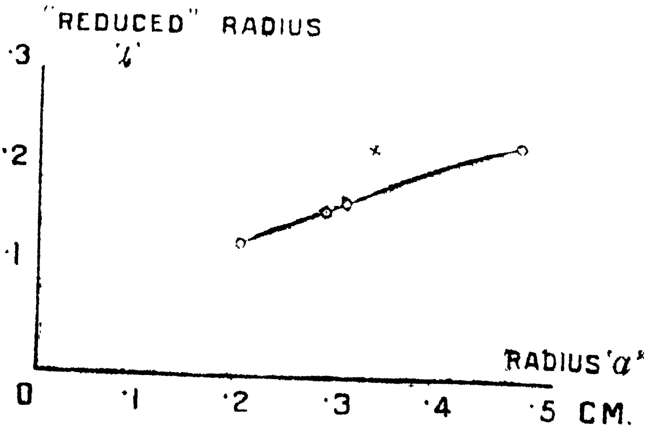

FIG. 2.

The values of 'a' are plotted against those of 'b' on a graph paper—circles indicating the pairs of points for tubes with vertical arms and cross for that of inclined arms. It is seen that the former lie on a smooth curve while, as is to be expected, the latter lies out of the way. Making this reservation, the results conclusively show that for smaller diams. the corresponding reduced diams. are proportionately larger.

5. *Summary and Conclusions.*

(1) A new method for comparing viscosities of different liquids is described.

(2) It is shown that if equal lengths of liquid columns are taken into a bent tube the log. decrements of the oscillations in the tube are directly proportional to their kinemetic coefficients of viscosity.

(3) Experiments conducted with five tubes and seven different liquids are found to give remarkably consistent and accurate results.

In conclusion I wish to offer my sincere thanks to Drs. C. V. Raman, F.R.S. and A. L. Narayan, F. Inst. P. for valuable suggestions and their continued interest in this work; I am also much indebted to Prof. S. Purushotham, M.A., under whose guidance the mathematics has been worked out.

Vizianagram.
11-12-26.

Some Results of Experimental Study of Substances having Considerable Internal Friction

BY

BORIS WEINBERG.

(PLATES IX, X AND XI)

The asymptotical reaching of final steady stage.

In my previous paper[1] I have shown the complexity of the phenomena, relating to the transformations of solids under the action of stresses exceeding the limit of elasticity as well as the imperfection of the methods adopted heretofore to the study of these phenomena. As an additional difficulty must be mentioned the difficulty of eliminating, *post factum*, the considerable influence of temperature (*4*; *53*, 244-245) varying unavoidably during the experiments in apartments but imperfectly protected against variations of temperature which had been made during the years 1903-15 by me and my co-workers and often have lasted several weeks if not months.

We were studying exclusively the four simplest regimes to which a solid can be subjected, namely

I. f (force) = const.;

II. x (deformation) = const. (relaxation);

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[1] *Boris Weinberg.* "On the Methodology of Studying the Slow Transformations of Solids—Proc. Ind. Ass. Cult. Science, *9*, 215-250, 1926. This paper shall be cited as N *53*, numbers *1-52* denoting the papers enumerated on its last four pages; the present paper shall bear N 54. I may add that the article *36* is now printed in extenso in the J. Russ. Phys. Soc., *58*, 33-40, 1926 and the article *50* in the Bull. Tomsk. Univ., 74, 1-2, 1924. The stereoscopic figures 4 and 6 which ought accompany the paper *53* and were omitted in the Vol. *9* of Proc. Ind. Ass. are attached to the present issue. (Plates IX and X)

III. $f=0$ (elastic after-effect);

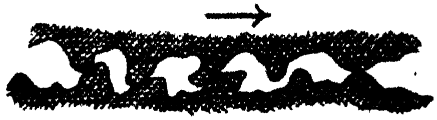
IV. $\frac{dx}{dt}=0$.

I personally have made 180 series of observations on regime I of total duration of 3012 days, 61 series (188 days) —on regime II, 101 series (1756 days)—on regime III, and 45 series (1499 days)—on regime IV.

From these 387 series (of total duration of 6455 days) I have till now—on account of above mentioned difficulties—discussed only a part of observations on regime I and IV and exclusively these stages of the experiments when the regime became approximately stationary. The reason of my delaying the discussion on the regimes II and III and on the initial stages of the regimes I and IV is—I must sincerely confess—the absence of a firm standpoint for such a discussion.

Even the theory of relaxation although only a formal and phenomenological one, can be applied to the initial stage of the regime I only by means of additional suppositions of independent relaxation of each elementary stress provoked by every new increase of deformation (*42* gives an attempt to form corresponding integral equation).

The supposition of molecular overjumps (*40*, *46*) along the gliding planes in a crystal or in a separate crystallite of a metal may give some hopes especially if we try to connect it with the observations of *Verchovskij* (*53*, 241-242; published now more fully in the J. Appl. Phys.) on deformations of solids before the beginning of their relative motion in the case of sliding "dry" friction as well as on the periodicity of this motion once started.



If we take as the point of issue for the explanation of the sliding dry friction the phenomenon which was observed by *Verchovskij* and can be illustrated by the fig. 1 (taken from one of my popular scientific papers, dated 1908) we must no more deal with the notion of the force of external friction or of the corresponding *co-efficient* but only with the notion of the energy spent on external friction or of the *work* necessary to bend microscopical elevations which form the surface of the mutually sliding bodies until these elevations slip over each other and then straighten themselves. The idea of starting by the notion of energy spent in external friction has given to *K. B. Weinberg* (*52*) the possibility based on experimental data obtained by him and *V. B. Weinberg* (*51*) of explaining the phenomenon of friction with self-smearing—the phenomenon so evident in the case of the slipperiness of ice and explained before in this case by *Reynolds*, myself (*9*) and others by the lowering of the melting-point owing to pressure. *K. B. Weinberg* has pointed out that the pressure by itself cannot melt ice and that the melting of ice is due to the *work* spent in moving the slides and transformed in heat; this heat gives rise to a layer of water and the internal friction in this layer is equal to the force which must be applied to the sledge.

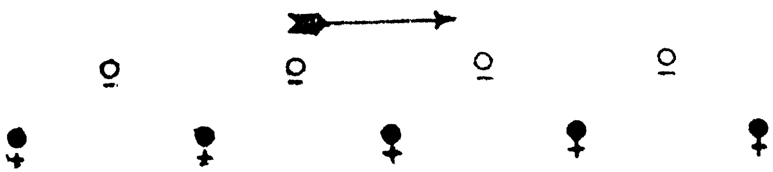


FIG. 2.

If we recur to an analogous idea in considering a layer of atoms in a sliding plane of a crystal or of a crystallite (fig. 2) we could probably understand the phenomenon of internal friction of crystals and construct an electrical theory relating to it in analogy with the electrical theory of elasticity of crystals. Such a theory could show a way to the explanation of internal friction of metals which are substantially conglomerates of differently orientated crystallites and also perhaps of liquids.

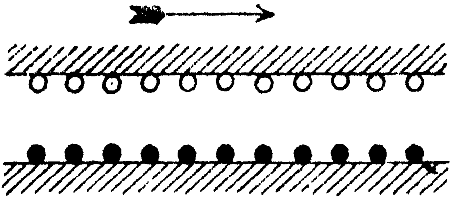


Fig. 3.

An intermediate stage would be the explanation of friction in a monomolecular layer separating two solid surfaces (fig. 3) as in the experiments of *W. B. Hardy & J. P. Hardy* (Phil. Mag. *38*, 32-55, 1919).

The internal friction of liquids explaining the external friction—sliding or rolling—of smeared surfaces, there would remain unexplained only one case of friction—the case of external rolling friction of dry solid bodies. My son *V. B. Weinberg* is trying now to work out a thermodynamic theory based on the presumed asymmetrical distribution of pressure on the area of contact between a plane *PP* (fig. 4) and the cylinder *C* which is rolling over it. This

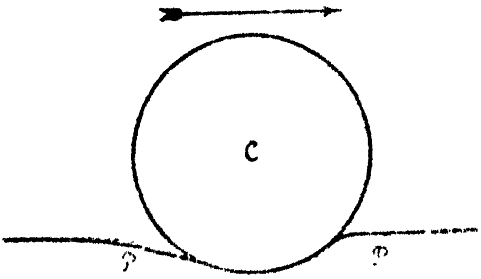
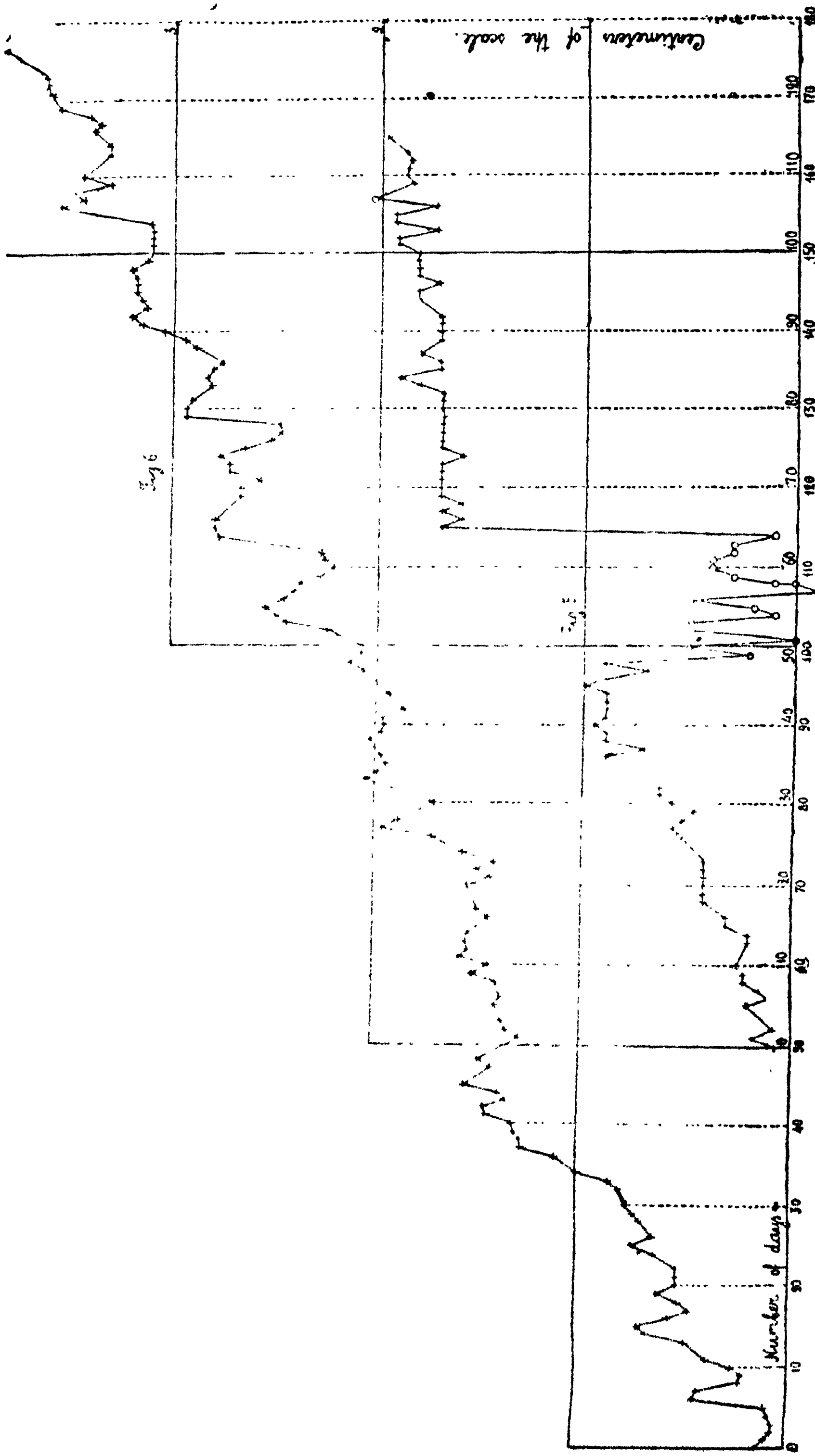


Fig. 4.

asymmetry (much exaggerated in fig. 4) must arise from the difference between the elastic polytropic compression of the front part of this area which is accompanied by a rise of temperature and the elastic polytropic expansion of the back part where must take place a fall of temperature.

Returning now to the final stages of my experiments on the regimes I and IV which were the object of the articles *3, 5, 8, 15* (ice); *13, 14, 17, 21, 23* (pitch); *40* (Iceland spar and rock salt) and *41* (lead), I must point out that the fundamental question is what is this final stage to which tends asymptotically the transformation. For regime I (f=const.) it may be $\frac{dx}{dt}$=const. or x=const., for regime IV ($\frac{dx}{dt}$=const.) it may respectively be f=const. or f=limit of plasticity.

The question is the more difficult to answer the greater are the forces of internal friction of the material which is the subject of our studies because the greater are these forces the longer is the interval of time after which the transformation may be considered as having reached its final asymptotical stage. When this interval is of the order of several weeks or months the influence of variations of temperature was screening in such a measure the differences between the attained stage and the final stage which we were looking for or the transformation was already so slow and difficult to be exactly followed that the decisive answer to the question was becoming a very hard thing. In other cases the big total value of the deformation was putting an end to the continuation of a series.


Centimeters of the scale.
Number of days
Fig 6
Fig 5
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
1
2
3

FIGS. 5 & 6.

But still in the most unfavourable circumstances the answer was for the first of the two alternatives mentioned above *i.e.*, for the constancy of final *velocity* of deformation in the regime of constant stress. This may be seen for instance from the figs. 5 and 6 which represent the result of a 115-days series on shearing a parallelopiped of iceland spar and of a 175-days series of shearing a parallelopiped of rock salt. Each point of these diagrams represents the mean of several readings of the divisions of the scale (distant 5·3 m. from the mirror) made during a day reduced to midday and to the mean temperature 18°·0 (extreme value 14°·5 and 20°·5 for the first series and 14°·3 and 23°·5 for the second); the circles denote doubtful values and the interruptions in the curves correspond to the cases of a probable or of an undoubtful displacement of the mirror relative to the parallelopiped. For spar the periods from $t=36$ to $t=48$ days and from $t=65$ to $t=115$ give mean shearing velocities $\phi'=1\cdot5$ and

$$0{\cdot}7.10^{-10} \quad \frac{\text{radian}}{\text{day}}$$

but even the second period (from which we obtain for the value of the co-efficient of internal friction

$$\eta=1\cdot5.10^{16}\ \frac{\text{gr.}}{\text{cm. sec.}}\ \Big)$$

cannot be taken as the steady final stage. For rock salt if we exclude the first three weeks we have for three equal parts of the remaining time $\phi'=3\cdot3$, $3\cdot3$ and

$$3.0.10^{-11}\,\frac{\text{radian}}{\text{day}}\Big(\ \eta=5\cdot7,\ \ 5\cdot7\ \text{ and }\ 6\cdot2.10^{16}\ \Big)$$

what can be considered as rather near approximation of the

For torsion of prisms of rock salt I shall give only an abridged table giving the mean deflections d (in tenths of a millimeter of a scale 525 cm. distant from the mirror) for each of 5-days intervals of a 177-days long series (*40*, 45-46):

TABLE I.

$t =$	5	15	25	35	45	55	65	75	85
$d =$	303	333	347	382	428	424	437	448	478
$t =$	95	105	115	125	135	145	155	165	175
$d =$	484	518	539	538	571	599	609	624	655

Even these smoothed values show such irregularities of the extremely slow displacement of the scale—in average about 0·2 mm. a day corresponding to shearing velocities ϕ' of the order 5.10^{-12}—that we can only with a certain probability say that the steady stage was reached (Δd for each successive 30 days from $t=55$ equal to 5·4, 6·1, 6·0 and 5·6 mm.). The corresponding value of η (for 20°) is $2{\cdot}3.10^{18}$—much greater than the values given above and corresponding to ϕ' some 6 times greater. Two other series (84 days and 714 days long) give $\eta=1{\cdot}8.10^{18}$ and $6{\cdot}2.10^{18}$ but during the last series readings of the scale and of the temperature were taken only at the beginning and at the end.

PLATE IX

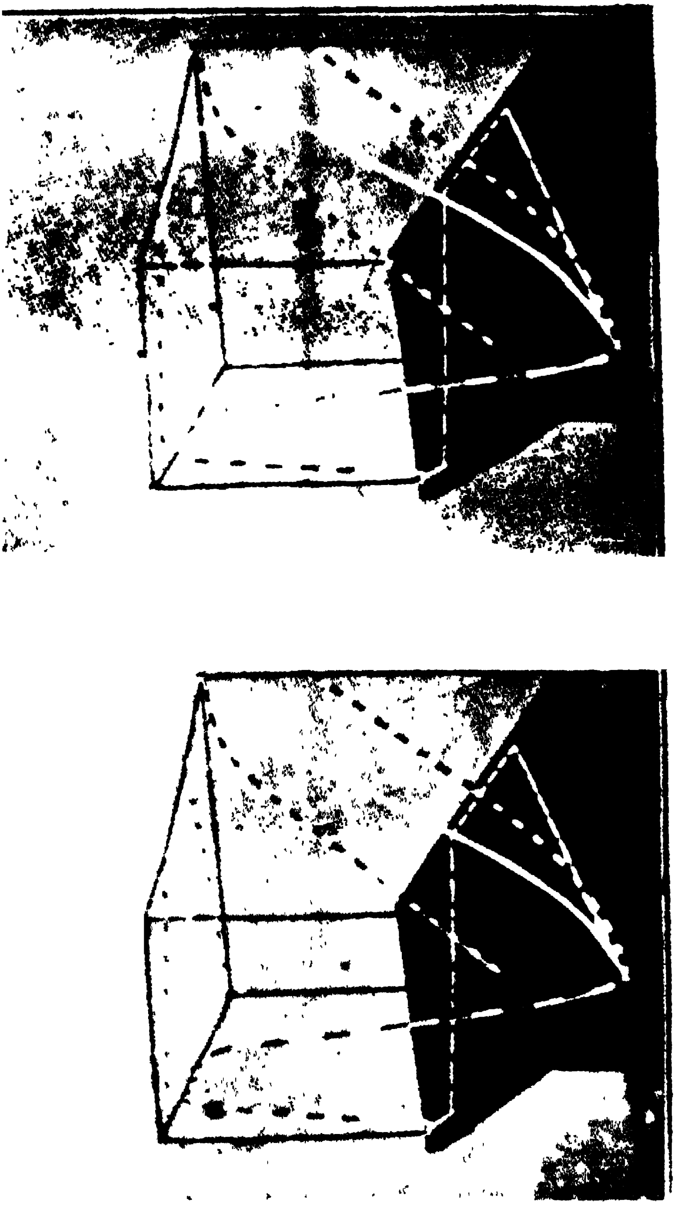


Fig. 4.

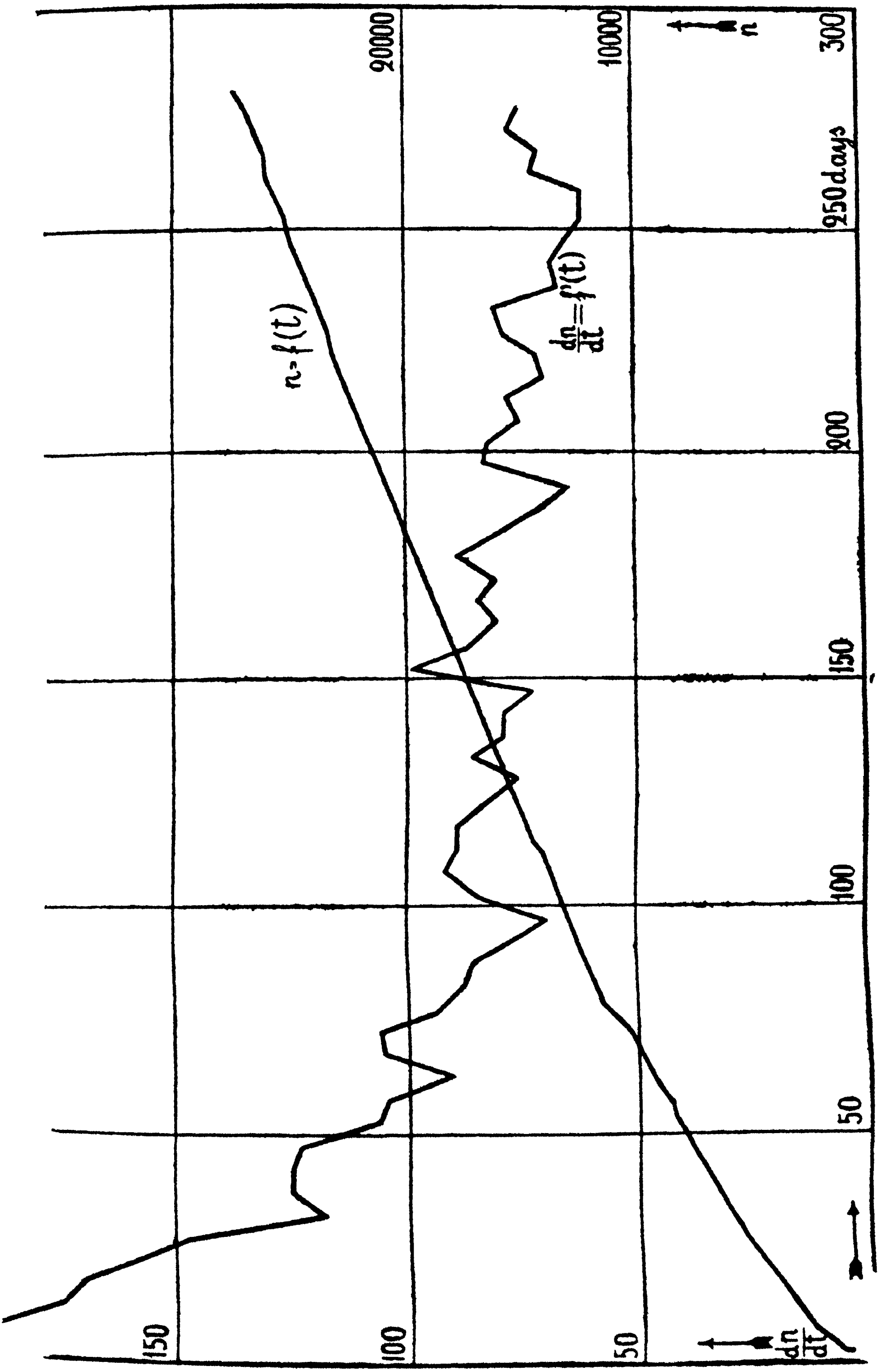

20000
10000
n
300
250 days
$n = f(t)$
$\frac{dn}{dt} = f'(t)$
200
150
100
50
150
100
50
$\frac{dn}{dt}$

Fig. 7.

I shall give here also a diagram corresponding to a 280-days long torsion of a thin lead tube (fig. 7). Here n denotes the divisions (in mm.) of scales which were successively—with corresponding telescopes—put around the tube at a distance of 181 cm. All the angular velocities were reduced to 20° by means of a formula (*4*, 184)

$$\Delta n_{20} = \Delta n_t 1{\cdot}03^{20-t} \qquad (1)$$

owing to the variability in the friction of pulleys and in the tension of the threads bearing the weights. The calculated mean value of $\frac{dn}{dt}$ only for successive 5-days intervals. The corresponding graph shows that after 2-3 months of an apparently constant $\frac{dn}{dt}$ the last month has given a sensible diminution of this quantity due probably to a partial local collapsing of the walls of the tube after it had suffered a total torsion of about 8 radians (the length of the tube was 269 cm.). The value of η from this series was $2{\cdot}5.10^{16}$ for $\phi' = 1{\cdot}8.10^{-10} \frac{rad.}{sec.} = 1{\cdot}6.10^{-5} \frac{rad.}{day.}$. Similar values—$2{\cdot}6$ and $2{\cdot}9.10^{16}$—of η were deduced from torsion (72 and 32 days) of this and another tube with $\phi' = 1{\cdot}2$ and $2{\cdot}3.10^{-10} \frac{rad.}{sec.}$ but lesser values—$1{\cdot}0, 1{\cdot}4$ and $1{\cdot}0.10^{16}$—from shearing a parallelopiped (76 and 27 days) and from torsion of the second tube (292 days) with $\phi' = 0{\cdot}8$, $1{\cdot}1$ and $2{\cdot}3.10^{-9} \frac{rad.}{sec.}$.

For substances having an η of a smaller order the final steady stage is reached much quicker—*e.g.*, for ice (η of the order 10^{13}) in several hours or a couple of days. This circumstance gave me the possibility to build up a theory of motion of ice in glaciers (*5*, *6*) and to verify it by comparing the values of η obtained by direct experiments and from the measurements of velocity of different points of the glacier Hintereis (Tyrol)—the only one for which the form of the bed and the thickness of ice were determined by direct boring. This theory can be in brief thus formulated: the bed of a glacier is for the ice a sort of capillary channel along the bottom of which the ice slides as a single solid body in mean time being deformed as a typical plastic body. The experimental value of η was $(1{\cdot}74 \mp 1{\cdot}10).\ 10^{13}$ (*5*, 360[1]) and the theoretical—$(1{\cdot}75 \mp 0{\cdot}70).\ 10^{13}$ (*13*, 175), the coincidence, if we pay attention to the great probable errors, must be considered as fortuitous.

Numerical data of the co-efficient of internal friction.

If we attain the final stationary stage of a transformation we can use the second or the third definitions of the co-efficient of internal friction (*53*, 235) of a plastic substance. Owing to experimental difficulties of determining η for substances for which the order of this quantity is high, to the considerable influence of temperature, to the incertitude of their chemical composition (most of typical plastic substances being no definite chemical compounds) and to the dependence of the value of η on previous mechanical and thermic treatment it is useless to communicate precise numerical values of η but only their order. If for instance we melt the substance without extreme precautions and a part of its volatile components is evaporated the value of η increases notably. This considerable influence of the composition of a mixture—especially for a binary compound (*31*)—makes the study of this constant of the "viscosimetry" of plastic substances—a powerful method of physical chemistry so emphatically recommended by one of the creators of this method *N. S. Kurnakov.*[1]

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[1] By mistake the pagination of the last part of the paper *5* is indicated (*58*, 247) 289—301 instead of 289—364.

In table II, I am confronting some numerical data extracted partly from my investigations, partly from the investigations of my co-workers or other authors who have used methods—more or less—satisfying to the conditions of invariability of volume and of the steadiness of regime. The methods are indicated by numbers corresponding to their previous enumeration (*53*, 231-234).

TABLE II.

No.	Substance.	Author.	Source.	Method.	t°C.	$\eta \frac{\text{gr.}}{\text{cm. sec.}}$
1	Molasses ...	Alhazor and Korostelev	*38*	7	18	$2 \cdot 2.10^3$
2	Venician turpentine	Ladenburg ...	Ann. d. Phys. *22*, 287, 1907.	9	?	$1 \cdot 3.10^3$
3			ditto ...	14	?	$1 \cdot 3.10^3$
4	Shoemaker's pitch with grease	Trouton ...	Proc. R. Soc. *77*, 426, 1906.	9	7	$2 \cdot 6-2 \cdot 8.10^5$
5			ditto ...	11	?	$3 \cdot 1.10^5$
6			ditto ...	12	?	$2 \cdot 5.10^5$
7	Shoemaker's pitch	,, ...	ditto ...	1	?	$2 \cdot 0.10^6$
8			ditto ...	11	?	$2 \cdot 0.10^6$
9	Shoemaker's pitch with turpentine oil	Reiger ...	Ann. d. Phys. *19*, 999-1002, 1906.	10	10	$0 \cdot 9.10^9$
10			ditto	10	10	$1 \cdot 2.10^9$
11			ditto ...	10	10	$1 \cdot 3.10^9$

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[1] See *e.g.*, the last sentences of the article cited in the note 4, p. 234, No. *53*.

TABLE II—*(contd.)*

No.	Substance.	Author.	Source.	Method.	t°C.	$\eta \ \frac{\text{gr.}}{\text{cm. sec.}}$
12	Shoemaker's pitch	Obermayer	Sitz. Wien, Akad, *75*, 677, 1877.	10	12	2·7.10^{8}
13			Sitz. Wien, Akad, *75*, 677, 1877.	1	15	0·9.10^{8}
14			Sitz. Wien, Akad, *75*, 674, 1877.	3	15	1·0.10^{8}
15			Sitz. Wien, Akad, *113*, IIa, 538, 1904.	3	20	1·4.10^{8}
16		Trouton	l. c.	1	?	1·0–1·4.10^{10}
17			ditto	11	?	1·1.10^{10}
18			ditto	12	?	1·2–1·4.10^{10}
19		Weinberg & Smiznov.	9 and 10, *19*, 33	2	20	1·7–3·1.10^{8}
20			... ..	6	20	0·9–2·0.10^{8}
21			......	3	20	1·1–2·8.10^{8}
22			... .	1	0	4·8.10^{12}
23		Weinberg	*18*, 175	8	?	1·9–2·0.10^{7}
24			*21*, 211	2	15	2·0.10^{8}
25			ditto	2	50	1·6.10^{4}
26			*23*, 255	8	?	5·6–8·4.10^{6}
27		Jostjunin & Le-Dentu.	*22*, 249	7	20	8·8.10^{7}
28	Asphalt	Weinberg	*21*, 223	2	15	3·1.10^{10}
29			,, ,,	2	50	1·2.10^{8}
30			*21*, 228	6	15	2·5.10^{10}
31		Miloradov & Jolmacev.	*26*, 512	1	18	1·4–4·8.10^{10}
32		Dudeckij	*29*, 529	4	15	8·1.10^{10}
33			,, 533	5	15	8·8.10^{10}

TABLE II—(*concld.*)

No.	Substance.	Author.	Source.	Method.	t°C.	$\eta \frac{\text{g.}}{\text{cm. sec.}}$
34	Sealing wax	Segel ...	Phys. Zeits. *4*, 494, 1903.	6	19	$1\cdot1.10^{10}$
35	Stearate of sodium	Trouton & Andrews	Proc. R. Soc. *19*, 57, 1904.	1	8	$5\cdot0.10^{11}$
36	Menthol ...	Haydweiller ..	Ann. d. Phys. *63*, 59, 1897.	10	15	$2\cdot0.10^{12}$
37			ditto ...	10	39	$2\cdot5.10^{9}$
38	Ice of Neva ...	Weinberg ...	*5*, 275 ..	1	14	$8\cdot5.10^{13}$
39			,, ,, ..	1	0	$1\cdot0.10^{13}$
40	Ice of Hintereis ferner		,, 321 ..	1	5	$1\cdot9.10^{13}$
41			,, ,, ...	1	0	$0\cdot5.10^{13}$
42	Glass ...	Trouton & Andrews.	l. c. ...	1	575	$1\cdot1.10^{13}$
43			ditto ...	1	710	$4\cdot5.10^{10}$
44	Colophonium .	Reiger ...	Phys. Zeits. *2*, 215, 1901.	15	12	1.10^{17}
45			ditto ...	15	30	$1\cdot4-1\cdot7.10^{14}$
46			ditto ...	15	46	$2\cdot5-3\cdot0.10^{12}$
47	Lead ..	Weinberg ...	*41*, 33 ..	3	20	$0\cdot6-1\cdot2.10^{16}$
48			,, ,, ...	1	20	$0\cdot9-1\cdot6.10^{16}$
49	Iceland spar .		*40*, 44 .	3	18	$1\cdot5.10^{16}$
50	Rock salt ...		,, ,, ...	3	18	$6\cdot2.10^{16}$
51			,, 45 ...	1	18	$1\cdot8-2\cdot3.10^{18}$
52			,, ,, ...	1	81	$2\cdot6.10^{17}$

The values of η were, when possible, reduced to an infinitely great velocity of shearing by means of the law of *Schwedoff* [53, 228, (26)].

Practical realization of different methods of determining η.

I shall pass now to a closer examination of the different methods which have been applied by me and my co-workers for determining η and shall give here more detailed numerical data than in the table II as well as the formulae used for their calculation in the assumption that the substance obeys the law of *Schwedoff.* From the latter we can easily—in making δ (the limit of elasticity) equal to zero—obtain the formulae applicable to a substance obeying the law of *Maxwell* and I would like to add here that such formulae can be deduced from the corresponding formulae of the theory of elasticity by replacing N (modulus of rigidity) by η and α (angle of shear) by α'.

I venture two precursory general remarks.

1. In most of the methods it is the variation of an angle which has to be observed, but if even the object of measurements is a linear velocity the most efficient is the use of scale and mirror. Assuming 0·2 mm. as the limit of precision in determining the difference between two consecutive readings of a scale distant 5 m. from the mirror and taking a day as a natural maximal interval of time between two readings we come to an angular velocity of the order $10^{-10}\,\frac{\text{rad.}}{\text{sec.}}$ as the minimum which we can establish with certainty and as the maximal precision with which an angular velocity can be measured.

In dealing with such small angular velocities special precautions are needed what concerns the immobility of the supports of the scale, of the telescope and of the mirror. Almost indispensable is then the use of a second controlling mirror invariably connected with the supports. As to the methods of attaching the mirrors to the samples, special comparative observations made by me during the experiment on shearing lead parallelopipeds, have shown that the mirrors pasted with ordinary wax, with sealing wax or with

Mendeleev's paste, or firmly fixed in metallic mountings give identical—to $10^{-10}\frac{\text{rad.}}{\text{sec.}}$—results. If such is the precision of evaluation of minimal angular velocities the methods 3—6 where we can indifferently measure angular velocities or relative linear velocities of motion of one layer relative to another, the distance between the layers not exceeding 5—6 cm., give in the first case the possibility of stating the existence of a linear velocity of an order $10^{-8}\frac{\text{mm.}}{\text{sec.}}$. If on the contrary a small linear velocity is measured by a microscope and if we assume 0·05 mm. as the limit of precision in the evaluation of a difference between two consecutive readings of the microscope at a day's interval the minimal observable linear velocity is only $6.10^{-7}\frac{\text{mm.}}{\text{sec.}}$.

In the cases of greater angular or linear velocities the scale and mirror method can lose its preferability, its precision and sensibility becoming superfluous. When the velocities are still greater, the interval between two readings must be correspondingly diminished, but it is difficult to reduce it under a minute, if we wish to have a precision of 1%, without recurring to automatic registering.

2. Except the methods 4 and 6 where we can apply stresses directed vertically downwards and the methods 7 and 8 where the weight of the body is the acting force we have to use pulleys if we wish to use the force of gravity, which has the merit of being constant. A pulley as I have already considered (*53*, 242) effaces in a certain measure this merit making the acting force to oscillate between the values $P-q$ and $P+q$ where P is the weight of the suspended mass and the q—the maximal forces of friction. This defect became evident only gradually and in the later investigations we were using special pulleys of greater radii and on ball-bearings. For greater velocities this defect was of secondary influence; for instance in my experiments on internal friction of pitch and asphalt (*21*) the q could attain 30% of P but the variations

PLATE X

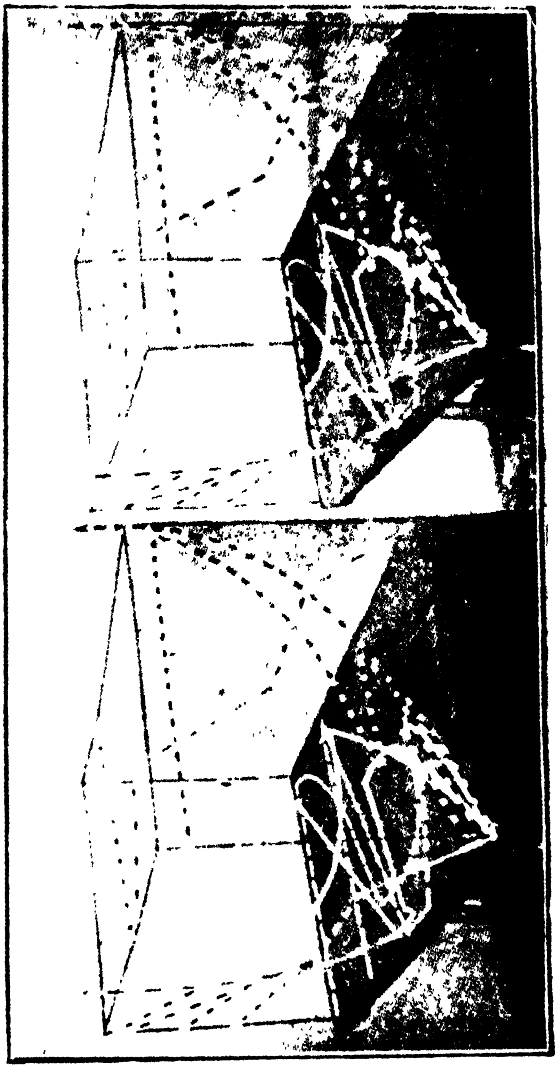


Fig 6

of the velocity at the same temperature did never exceed some 10—15%.

In the experiments of *Kuznecov* (28) and *Dudeckij* (29) q was reduced to 0·5—1% that is to the limits of precision of observations which are set by the enormous influence of temperature and the small thermo-conductivity of the studied substances.

1. *Simple or helicoidal torsion.* The method is especially adapted for the metals because in this case we can take a long and thin wire (suspended vertically) and thus have big values of the quotient ϕ (angle of torsion): α_{max} (maximal angle of shear) which is equal to the quotient l (length): r (radius of the wire). For other substances the sensibility is less because the axis of the cylinder can no more be vertical and its horizontality does not allow to have big values of $l:r$. Even for $l:r=10$—15 in the case of such substances as pitch and asphalt which are yielding under their own weight we have to use supporting baths of mercury.

If we denote by FR the moment of the torsional forces we have (5,276).

$$\eta_{\propto}\ \frac{gr}{cm.\ sec}=\left(\frac{2FRl}{\pi r^4}-\frac{4l\delta}{3r}\right)\frac{1}{\phi'} \qquad \ldots \quad (2)$$

This formula must be applied if the observation shows that the co-efficient η of internal friction computed by means of the ordinary formula

$$\eta=\frac{2FRl}{\pi r^4\phi'} \qquad \ldots \quad (3)$$

is not constant but varies linearly with—

$$\frac{1}{\phi'},$$

namely by

$$\eta=a+\frac{b}{\phi'} \qquad \ldots \quad (4)$$

The determination of b (*e.g.* by means of the method of the least squares) gives the possibility of evaluating δ for such substances for which it is too small to be determined directly —*e.g.*, for ice for which I obtained

$$\delta = 5 \cdot 6.10^5 \frac{gr}{cm\ sec^2}$$

in the case of torsion of cylinders of Neva-ice in the directions perpendicular to the optical axis and $0 \cdot 3 \times 10^5$ for the ice of Hintereisferner.

The angle of torsion ϕ must correspond to the part of the cylinder or of the prism which is really twisted. If this angle is measured by the relative displacement of the two basal mountings of the twisted slab, we must be sure that the terminal parts of the slab are immovable relatively to these mountings. This immobilisation is difficult when we deal with crystals. For ice I overcame the difficulty in making the mountings with corresponding holes also from ice and in freezing the cylinders to the mountings by means of filling the interstices with abundantly moistened snow or a mixture of finely hatched ice and water. Rock salt slabs were fixed in mountings by means of molten alum.

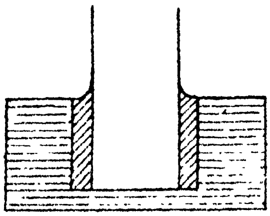


FIG. 8.

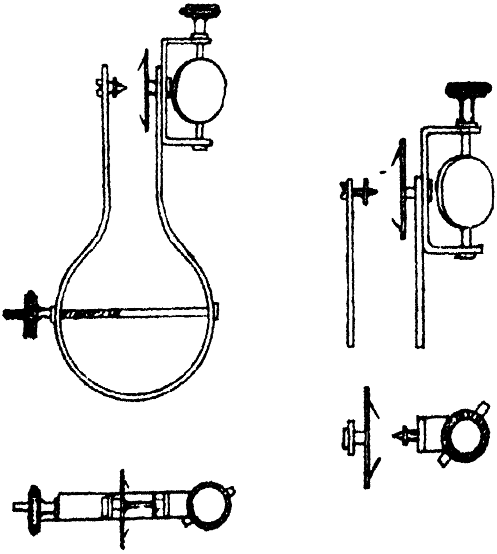


FIG. 9.

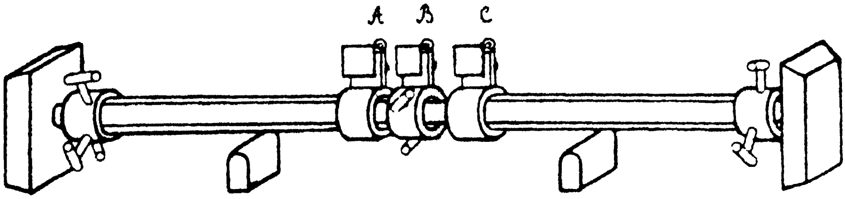


FIG. 10.

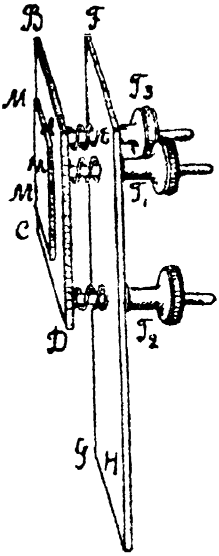
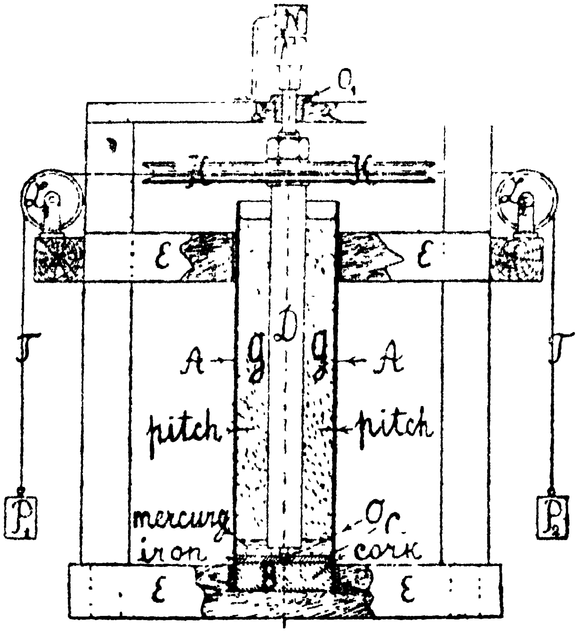


FIG. 11.

The presence of such an intermediate substance (fig. 8) making indeterminate the place of the layer which has to be considered as untwisted, it is preferable to fix the mirrors at some definite places of the slab itself. Fig. 9 represents the type of mountings which I used in experiments of twisting rather thin prisms of rock salt and which in allowing to direct easily the reflected rays into the telescope practically annulled the indetermination of the position of the layer the displacements of which were corresponding to the displacement of the mirror. Fig. 10 represents the method of measuring the angular displacement of two terminals and one middle layer of a lead tube by means of two glass tubes transmitting the two first displacements to the mirrors A and C. Fig. 11 gives the details of the mountings of the mirrors used in most of our experiments.

The method of helicoidal torsion was used by us in great many researches (ice, lead, copper, brass, iron, steel, rock salt, paraffin—*50*) as one especially fitted for elucidation of methodological questions and for preliminary explorations. Some of these researches were made for furnishing mechanical characteristics of compositions of asphalt rock, bitumen and gravel used for practical purposes.



.FIG. 12.

2. *Spiraliform torsion.*—The type of apparatus is clear from fig. 12, showing the apparatus which *Smirnow* and myself have used (*19*) in studying internal friction of pitch. Further

perfectionings consisted in diminution of external friction at the upper part and at the pulleys.

If we call r_0 and r_1 the radii of the cylindrical layer of the substance, h its height, FR the moment of torsional forces and ϕ' the angular velocity of the inner cylinder relative to the outer we have (*21*,224)

$$\eta_\infty = \left[\frac{FR}{2\pi h}\left(\frac{1}{r_1^2}-\frac{1}{r_0^2}\right) - \delta\, lg\,\frac{r_0}{r_1}\right]\frac{1}{\phi'} \qquad \dots \quad (5)$$

My experiments on pitch (21) show that the velocity ϕ' measured by the observed velocity v of the scale was very nearly proportional to F (consequently practically $\delta = 0$) as can be seen from Table III giving the logarithms of velocities v_1 reduced to the force of 1 gram (weight).

TABLE III.

$t°$ F. (gr)	15	20	30	40	50
10	...	...	$\bar{2}\cdot611$ $\mp\cdot055$	$1\cdot720$ $\mp\cdot061$	$0\,702$ $\mp\cdot054$
20	$\bar{4}\cdot602$ $\mp\cdot034$	$\bar{3}\cdot340$ $\mp\cdot041$	$\bar{2}\cdot657$ $\mp\cdot034$	$\bar{1}\cdot780$ $\mp\cdot041$	$0\cdot707$ $\mp\cdot029$
50	$\bar{4}\cdot590$ $\mp\cdot016$	$\bar{3}\cdot344$ $\mp\cdot061$	$\bar{2}\cdot641$ $\mp\cdot016$	... ...	... ...
70	...	$\bar{3}\cdot326$ $\mp\cdot014$	$\bar{2}\cdot637$ $\mp\cdot022$	... ...	... ...
150	$\bar{4}\cdot607$ $\mp\cdot026$	$\bar{3}\cdot340$ $\mp\cdot012$	... ...	... ...	... ...
Mean	$\bar{4}\cdot596$ $\mp\cdot013$	$\bar{3}\cdot335$ $\mp\cdot009$	$\bar{2}\cdot641$ $\mp\cdot013$	$\bar{1}\cdot761$ $\mp\cdot039$	$0\cdot706$ $\mp\cdot026$

From these values I have deduced for η the expression

$$\eta_t = (3{\cdot}81 \mp 0{\cdot}09)\ 10.^7 10^{-(0{\cdot}1408 \mp 0{\cdot}0004)\ (t-20) + (0{\cdot}00093 \mp 0{\cdot}00023)\ (t-20)^2} \qquad (6)$$

On the contrary the values of log v, for asphalt show an evident tendency to increase with F as can be seen for instance from the following data (relating to 15^0).

TABLE IV.

F.	100	200	400	600	900
Log v_1 … Obs. …	$\bar{6}{\cdot}549$	$\bar{6}{\cdot}676$	$\bar{6}{\cdot}713$	$\bar{6}{\cdot}755$	$\bar{6}{\cdot}757$
	$\mp{\cdot}045$	$\mp{\cdot}015$	$\mp{\cdot}025$	$\mp{\cdot}020$	$\mp{\cdot}015$
Log v_1 … Calc. …	$\bar{6}{\cdot}546$	$\bar{6}\ 677$	$\bar{6}{\cdot}730$	$\bar{6}{\cdot}746$	$\bar{6}{\cdot}756$
	$\mp{\cdot}024$	$\mp{\cdot}010$	$\mp{\cdot}007$	$\mp{\cdot}006$	$\mp{\cdot}006$

The last two lines were computed by assuming

$$v = \chi + Fy \qquad \ldots \quad (7)$$

what is analogous to the formula (4).

The values of y lead to the expression

$$(\eta_\infty)_t = (4{\cdot}76 \mp 0{\cdot}22){\cdot}10^9.10^{-(0{\cdot}1573 \mp 0{\cdot}0042)\ (t-20) + (0{\cdot}001236 \mp 0{\cdot}000286)\ (t-20)^2}$$

The values of δ which result from the values of χ in the formula (7) are rather uncertain so that only their order is of interest namely $4.10^2 \frac{\text{dyne}}{\text{cm}^2}$ at 15^0, 3.10^2 at 20^0 and 2.10^2 at 30^0.* From the measurements of *Miloradov* & *Tolmacev* (*26*, 12, Table III) who have obtained for η some 2—6 times greater values, we can compute for δ values ranging from 2 to $11.10^3 \frac{\text{dyne}}{\text{cm}^2}$. *Dudeckij* (*29*) who had η about 3

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*In my article (*21*, 225) I erroneously give 7.10^3, 6.10^3 and 8.10^3.

times as great as mine, finds for δ values $1\cdot8.10^{3}$ (method 4) and $1\cdot4.10^{3}$ (method 5). These differences must be attributed to different thermal treatment of the substance which has been identical in all the three cases. For the sake of comparison I shall mention, besides the data on ice given above, the following data relating to the limit of elasticity of some other plastic bodies: $1\cdot8.\ 10^{5}\ \frac{dyne}{cm^{2}}$ for wax at 10° (for extention) *Segel*,* $7\cdot0.\ 10^{4}$ for "mastics" (a composition of 10 weight-part of ground asphalt rock and 1 part of bitumen) *Monstrow (24)*, $3\cdot9.\ 10^{3}$ for a mixture of 3 parts "mastics" and 1 part of bitumen—*Monstrow-Weinberg* (*25*).

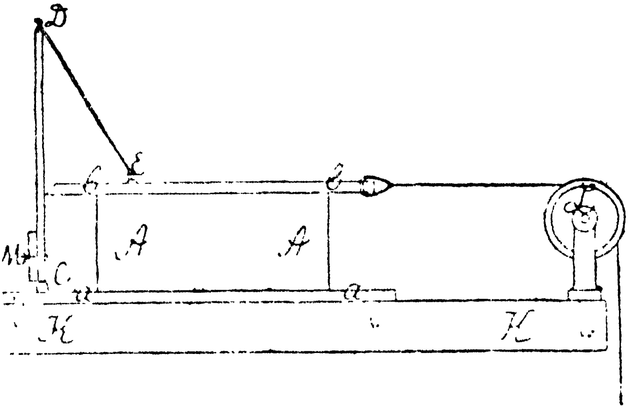

FIG. 13.

3. *Shearing of a parallelopiped.* Fig. 13 (*19*, 29) is sufficient for giving an idea of realisation of the method. The numerous defects of this method especially its moderate sensibility restrain its application and impel to use it only as extreme refuge,—*e.g.*, for stating the fact of the final constant velocity of deformation under constant stress in the case of *uniform* deformation of a crystal (iceland spar, rock salt) or of a metal (lead). We have had to recur to this

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* *M. J. Segel.* "An attempt to make use of interference fringes for studying the elasticity of soft bodies," Kazan, 1899, p. 89 (in Russian).

method also in studying mechanical properties of clay (*35*) a substance which in all other methods was sliding under stress over the solid walls of the vessel containing it or of the mountings which had to retain their outer surfaces. Only in using wooden plates pressed to the opposite sides of a parallelopiped of clay (30% of water) we could measure the deformations of the clay itself (the mirror was suspended on the upper one of the two knitting needles inserted in the clay horizontally and perpendicularly to the acting stress and was leaning on the lower needle by its lower part). The experiment has shown a rather quick plastic deformation of the clay after applying a stress but the velocity of the deformation was gradually diminishing and finally became equal to zero, after which the clay acquired the behaviour of an *elastic* body by the application or the taking off of any stress lower than the first one. The application of a greater stress caused again a plastic flow followed by a corresponding increase of the limit of elasticity analogous to the behaviour of most of the "soft" metals.

In this method η is calculated by means of the formula.

$$\propto = \left(\frac{F}{S} - \delta \right) \frac{1}{\phi'} \qquad \ldots \quad (8)$$

where S is the section of the parallelopiped and F the acting force.

4. *Shearing of two adjacent parallelopipeds.* Fig. 14 represents the apparatus used by *Dudeckij* (*29*) for asphalt. The distance of the plates (wooden with small deepenings to secure the immobility of the layers of asphalt contiguous to the wood) was chosen a little too big and the acting weight too small relatively to the weight of asphalt what has caused an exaggerated deviation from the uniformity of deformation. This may be seen in fig. 14 where the lower surface

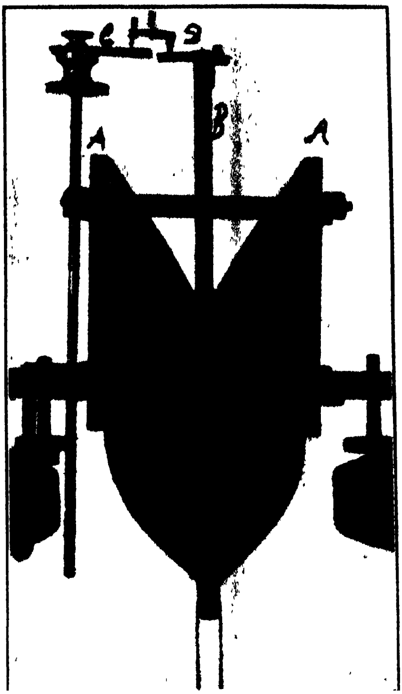
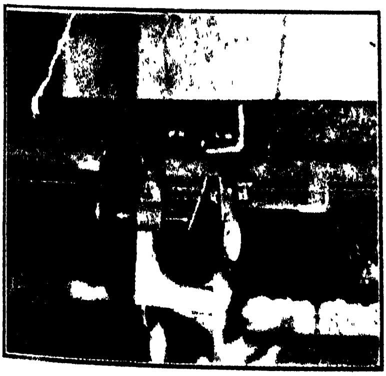


Fig. 14.



Fig

Fig. 16

has a form different from the form of the upper surface; this difference was compensated for by a contraction in the transverse direction which was clearly seen up to half the height of the parallelopipeds.

If we denote by v the velocity of a vertical layer situated at a distance l from the fixed plate, by R the distance between one of the fixed plates AA and the middle one B, by P the mass of the acting weight, by Δ the density of asphalt, by S the section of asphalt, we have the differential equation

$$\tfrac{1}{2}\mathrm{P}g+\mathrm{S}\Delta g(\mathrm{R}-l)=\eta_{\infty}\mathrm{S}\frac{dv}{dl}+\delta\mathrm{S} \qquad \ldots \quad (9)$$

which, integrated between the limits $l=0$ and $l=\mathrm{R}$ (and consequently $v=0$ and $v=\mathrm{V}$, where V, is the velocity of the middle plate), gives, if we denote by P the mass of one of the asphalt parallelopipeds,

$$\eta_{\infty}=\frac{(\mathrm{P}+p)g\mathrm{R}}{2\mathrm{S}v}-\frac{\delta\mathrm{R}}{v} \qquad \ldots \quad (10)$$

The equation (9) shows that v must increase as we approach the fixed plates. The velocity V was measured by means of an optical lever D the left (on the fig. 14) point of which could be lowered when necessary by means of a micrometer screw.

The experiments which continued more than two months gave from the observations during first 1½ months when the nonuniformity of deformation was small, for the value of η_a and δ at 15°.

$$\eta_{\infty}=(8{\cdot}07\mp0{\cdot}03)10^{10},\ \delta=(1{\cdot}8\mp1).10^{6} \qquad \ldots \quad (11)$$

The values of η calculated from the formula (10) by assuming $\delta=0$ were at different velocities equal to 10·10, 9·16 and $8 \cdot 72 \cdot 10^{10}$ and the values from the formulæ (10) and (11) together were $10 \cdot 08$, $9 \cdot 23$ and $8 \cdot 69.\ 10^{10}$.

5. *Shearing of a tore* was realised also by *Dudeckij* (*29*). The upper circular wooden plate with a consolidating iron mounting was suspended by three wires to a single wire passing over a pulley and bearing on the other side a counter-balancing weight. The mirror serving to measure the angular velocity ϕ_R of shearing of the outer circumference of the tore was set on a heavy rider (fig. 15) reposing on a blade of a knife fixed to the mounting of the upper plate. The other arm of the rider was leaning against the end of a micrometer screw in order to displace the mirror when the end of the scale was coming to the middle of the field of vision of the telescope. An analogous displacement could be attained by displacing the knife relatively to the mounting.

If we call H the height of the tore, R and ρ its two radii, P the mass of suspended weights and ϕ_r the angular velocity of shearing at the distance r from the axis of the tore we have

$$'= \frac{R+\rho}{2}\, g = \int^{R} (\eta_\infty \phi + \lambda)\pi r^2 dr = \int^{R} \left(\frac{\eta_\infty \pi r^3 \phi_R}{R} + \lambda \pi r^2 \right) dr \qquad (12)$$

whence if in the first member we make $\rho = R$

$$,= \frac{4PR^2 g}{\pi(R^4 - \rho^4)\phi_R} - \frac{4\lambda R(R^3 - \rho^3)}{3(R^4 - \rho^4)\phi_R} \quad \ldots \quad (13)$$

The observations give [1]

$$\eta_\infty = (8{\cdot}79 \mp 0{\cdot}02).10^{10}, \quad \delta = (14 \mp 1).\ 10^{9} \quad \ldots \quad (14)$$

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[1] *Dudeckij* gives erroneously other figures.

the observed values of η for different values of ϕ being 10·47, 9·76 and 9·21.10^{10} whilst the values calculated by means of (13) and (14) were 10·47, 9·73 and 9·23.10^{10}.

6. *Axial shearing of a cylindrical layer.* The realisation is simple but the results of my measurements on pitch (19) were not quite satisfactory on account of perturbances caused evidently by thermic influences. There is *e.g.*, a series of observed velocities (in thousandths of a division of the ocular micrometer screw per hour) reduced all to 15°

TABLE V.

Date.	Temperature.	Velocity.
21,6,11—27,6,11	15·9—16·5	136; 152; 141
27,6,11—1,7,11	16·5—17·1	146; 202; 148; 148; 156; 142
1,7,11—6,7,11	17·6—17·9	135; 149; 152
6,7,11—11,7,11	17·3—18·1	149; 153

After this initial period of approximate unvariability the velocity began to rise and its increase can be well expressed by the formula

$$v\,(\,s_{max}\,-s\,)=v_0 l \qquad (15)$$

where v_0—is the initial velocity, l—the length of the cylindrical layer, s—the displacement of the inner cylinder corresponding to the epoch when the velocity was v and s_{max} —the displacement corresponding to the rupture—so that the difference s_{max} —s is the length of the part of the cylindrical layer which was holding then the inner cylinder (*cf.* 53,239, fig. 16). Table VI gives the mean velocities v_{obs} observed during this second stage as well as the mean velocities $v_{calc.}$ calculated by means of the formula (15)—all reduced also to 15°.

TABLE VI.

Date	11,7		15,7		20,7		26,7		2,8		8,8		13,8		18,8		23,8		27,8
$\bar{v}_{obs}$		158		175		175		186		203		227		243		301		272	
$\bar{v}_{calc.}$		175		178		180		191		208		225		240		255		269	
Date	27,8		31,8		4,9		8,9		12,9		16,9		19,9		22,9		25,9		26,9
v_{obs}		273		299		312		848		349		400		431		456		479	
$v_{calc.}$		281		295		311		332		352		384		424		462		492	

For the last three days—the rupture took place in the evening of 29 September—the constants of the formula (15) had to be changed in order to represent the motion.

The value of η_∞ can be computed from the formula (*19*,228)

$$\eta_\infty = \left[\frac{P - \pi R^2 lg\Delta}{2\pi l}\, lg\frac{R}{r} + \frac{R^2 - r^2}{4}\, g\Delta - \delta(R - r) \right] \qquad \dots (16)$$

where P is the mass of the acting weight, R and r—the outer and inner radii, l the length, Δ—the density of the deformed layer and v the velocity of the inner cylinder.

7. *Flow in a tube under the action of gravity.* I shall first deduce the formula which should be appliable to substances obeying to the law of *Schwedoff*. If we denote by v the velocity at a distance r from the axis of the tube and by p the gradient of pressure which in the case of a vertical tube is equal to $g\Delta$ we have for a unit of length of a layer comprised between two cylindrical surfaces of radii $r + dr$ and r

$$\left[\eta_\infty + \left(\frac{\delta}{\frac{dv}{dr}}\right)_r\right]\left(\frac{dv}{dr}\right)_r 2\pi r - \left[\eta_\infty + \left(\frac{\delta}{\frac{dv}{dr}}\right)_{r+dr}\right]\left(\frac{dv}{dr}\right)_{r+dr} 2\pi(r+dr)$$

$$= p2\pi r dr \qquad \dots (17)$$

whence in succession we obtain

$$-\eta_\infty d\left(r\frac{dv}{dr}\right)+\delta dr=prdr \quad \dots \quad (18)$$

$$-\eta_\infty r\frac{dv}{dr}=\tfrac{1}{2}pr^2-dr \quad \dots \quad (19)$$

$$\eta_\infty v=\frac{p}{4}(\mathrm{R}^2-r^2)-\delta(\mathrm{R}-r) \quad (20)$$

$$\eta_\infty v_{max}=\frac{p}{4}\mathrm{R}^2-\delta\mathrm{R} \quad \dots \quad (21)$$

$$\eta_\infty q=\int^{\infty}\left[\frac{p}{4}(\mathrm{R}^2-r^2)-\delta(\mathrm{R}-r)\right]2\pi rdr=\frac{\pi p\mathrm{R}^4}{8}-\frac{\pi\delta\mathrm{R}^3}{3} \quad \dots \quad (22)$$

where *g* is the volume of substance which flows out in a unit of time. The supposition $\delta=0$ gives the *Poiseuille's* formula.

The formula (19) shows that if

$$\tfrac{1}{2}p\mathrm{R}<\delta \quad \text{or} \quad \mathrm{R}<\frac{2\delta}{g\Delta} \quad \dots \quad (23)$$

no flow can take place.

According to circumstances we can use the formula (20) or (21) or (22). In the Table I the results 9, 10 and 11 of *Reiger* were obtained in these three ways.

I shall note that for tubes of a sufficiently big diameter we can for typical plastic bodies take no account of the normal pressure at the lower extremity of the cylinder if its length is sufficiently big because the surface tension of such substances is probably small. Indeed *Ignatiev* (*20*) in measuring the form of plane drops of " solid " pitch which they assumed after three months in a room where extreme values of temperature were 14° and 24° obtained α $3{\cdot}1\frac{mgr}{mm}$.[1] This value gives as the maximal normal pressure at the lower extremity of a tube of $r = 5$ mm. the value $1{\cdot}2\ \frac{\text{dyne}}{\text{cm}}{}_2$ which is very little in comparison on the "pitch-static" pressure of a column even a decimeter high.

From the results obtained by us by means of the method 7, I shall mention the observations of *Gostjunin & Le Dentu* (*22*) on the flow of pitch out of the "pitch-dynamic" tube (R = 10 cm., L = 316 cm.). The theoretical distribution of displacements (in cms) at different distances r from the axis and the observed displacements were, for instance, after 2½ hours of the outflow as follows.

TABLE VIII.

=	0·0R	0·1R	0·2R	0·3R	0·4R	0·5R	0·6R	0·7R	0·8R
δ_{obs} =	2·80	2·87	2·84	2·74	2·57	2·34	1·78	1·45	1·15
δ_{calc} =	2·83	2·80	2·72	2·58	2·38	2·13	1·81	1·44	1·02

The theoretical distribution was computed by means of the value (27) of the Table I which is the result of all the observations. The agreement is rather satisfactory if we take into account the difficulty of securing the lower surface of the pitch plane at the beginning of the experiment on an area 20 cm. in diameter (the final drop fig. 16 from this peculiar "capillary tube" weighed some 30 kg.).

For current determinations of η for substances with smaller values of this co-efficient, were used ordinarily following apparatus and methods. A straight strip (for instance the blunt side of a knife) is covered by a piece of of paper by means of which all the excess of "liquid" hanging at the lower extremity of the flow-tube (fig. 17) is

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[1] That has been the first determination of the surface tension of a "solid" body. My attempt (1896-1905) to repeat the *Plateau's* experiment with a sharp-edged piece of solid pitch which has been during nine years suspended freely in a saltpetre-solution of equal density and had assumed a nearly spherical form having only proved the existence of such a tension.

FIG. 17.

taken off (this flow-tube is screwed into the bottom of a larger cylindrical vessel filled with the substance). After sufficient time the excess of substance which flowed out of the tube is again taken off and the piece of paper with it (counterbalanced by an equal piece) plus all the drops (if any) which fell meantime are weighed. By means of the quantity of substance which has flown it is easy to calculate the height H_1 of it in the upper vessel at the end of experiment and then the gradient of pressure in the flow-tube is

$$p = g \Delta \frac{\frac{1}{2}(H_1 + K_1) + l}{l}$$

As an example I shall give here (see Table VIII) the results of determinations of *Rezninov* (33) on different mixtures of dammar-resin with turpentine oil the value of η for each mixture being the result of several experiments in most cases with two tubes of different radii.

TABLE VIII.

% of dammar =	0	30	50	60	65	70	75	80	85	90	95
$\eta_{22 \cdot 2}$ =	$1 \cdot 38 \cdot 10^{-2}$	$9 \cdot 97 \cdot 10^{-2}$	1·19	12·5	52·7	718	8640	$5 \cdot 19 \cdot 10^{5}$	$9 \cdot 56 \cdot 10^{7}$	$(1 \cdot 4 \cdot 10^{9})$	$(1 \cdot 2 \cdot 10^{10})$

The two last values are the result of 4-years flowing out of drops (weight 19·7 and 39·1 g, D=1·54 and 3·25 cm.) at room-temperature. The very rapid increase of η in this double-system is analogous to the increase of η for mixtures of colophonium with turpentine oil investigated by *Glaser*[1] as can be seen from the fig. 18 where the full line represents Log η according to *Reznikow* and the dotted one the results of *Glaser*.

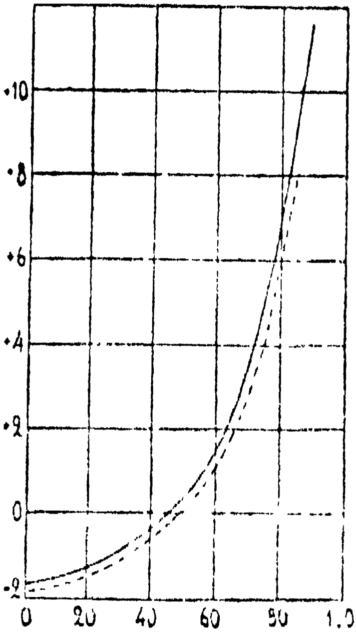

FIG. 18.

Flow in an inclined channel under the action of gravity. This method being more applicable to the study of the laminar motion of viscous liquids than to determination of η (*13, 14, 15, 23*) it shall be treated in the next paper which shall be devoted to this question.

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[1] Ann. d. Phys. 22, 694, 1907.

16

The Generalised Law of Vibration of Bowed Strings.

BY

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1. Introduction.

When a string is bowed in a suitable manner not far from one end, the vibration at any point on the string is found to be representable by a two-step zig-zag curve. This fact was discovered long ago by Helmholtz with his vibration microscope. He also found that the times occupied in the up-and-down-movements represented by the zig-zag curve are to one another in the same ratio as the two sections of the string which lie on either side of the observed point. Each point of the string moves with constant velocities, but the velocities at different points are different, being in fact proportional to its distances from the two ends of the string. In the special cases in which the bow is applied exactly at a point of aliquot division such as, $\frac{1}{2}$ or $\frac{1}{3}$ or $\frac{1}{4}$ or $\frac{1}{5}$ etc., of the length of the string from the end, the vibration-forms observed can be derived from the Helmholtzian mode of vibration by the omission of the harmonics having a node at the bowed point. Krigar-Menzel and Raps verified these results by photographic methods and found also that when the string is bowed at certain of the important nodal points dividing the string in such simple ratios as $\frac{2}{5}$ or $\frac{2}{7}$ or $\frac{2}{9}$ or $\frac{3}{8}$ the ratio of the velocities of ascent and descent was equal to $\frac{1}{5}$ or $\frac{1}{7}$ or $\frac{1}{9}$ or $\frac{1}{8}$ as the case may be, the vibration being no longer of the Helmholtzian type. They could not however discover any general law applicable to bowing at any arbitrary point on the string. Raman[1] discussed the nature of the vibration of bowed strings in a very general manner. He classified the principal types of vibration into vibrations of the first type, second type, third type, fourth type and so on, according to the number of discontinuities in the velocity-diagram of the string. The first type of vibration has got one discontinuity, the second type has got two, the third has three and so on. The Helmholtzian vibrations are those of the first type. The result of his investigation may be summed up in the equation

$$\frac{V_1}{V_2} = \frac{x}{l/n - x}$$

where V_1 = the velocity of ascent of bowed point
V_2 = the velocity of descent of bowed point
n = number of dis-continuities in the wave
x = distance of the bowed point form the nearest node of the n*th* harmonic
l = total length of string.

The present work has been undertaken to verify the general law of vibration of bowed strings enunciated by Raman, and also to find out the relation of the velocity of the bow to the motion of the bowed string. The cases, falling in the musical range of bowing in which the bow is applied at points intermediate between important nodal points, have also been specially investigated to find whether the Helmholtzian relation remains valid in such cases.

2. *Theory of String Vibration.*

Of the possible types of vibration set up by bowing a string, the simplest one is the vibration of the first type having one discontinuity on the velocity diagram. The velocity-diagram of the first type consists of a straight line passing through one end of string ($x = o$) with a discontinuity at the other end of the string ($x=l$). As the discontinuity moves in along the length of the string, the velocity-dragram consists of parallel lines passing through its two ends as shewn in the figure below.

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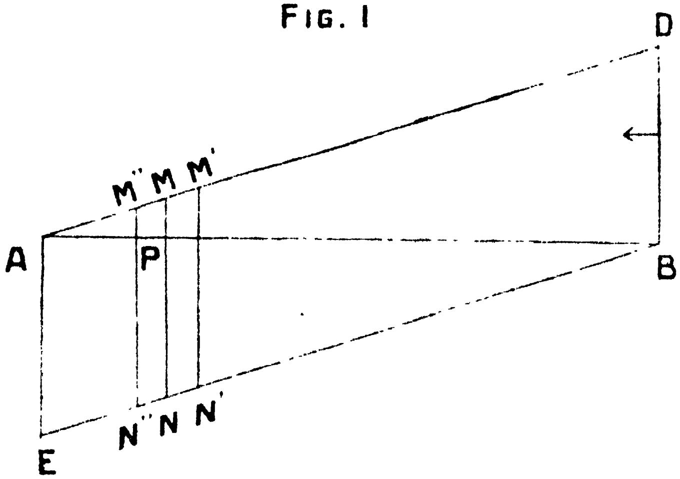
[1] C. V. Raman, Bulletin 15 of the Indian Association for the Cultivation of Science, 1918.

FIG. 1



In the above figure

AB=Length of the string
AD=Positive velocity line
BE=Negative velocity line
P =Any point on the string distant x from A
BD=Discontinuity at the end B of the string.

When the discontinuity lies at a point M′ between P and B on the string, the velocity-diagram of the point is given by the line AM′N′B and the point P has a velocity represented by the ordinate PM. When the discontinuity crosses P and moves between P and A, the velocity-diagram is represented by the line AM″N″B and the point P has a velocity given by the line PN. The vibration graph may be easily seen to be a two-step zig-zag curve. The motion of the point P during the full period of its vibration may be plotted by taking times as abscissae and the product of the time into velocity possessed by the point during the time as ordinates and by supposing the point to be displaced from its initial position through such ordinates at such times. For the sake of convenience, time may be made proportional to the length of the string along which the discontinuity travels. The nature of the curve traced may be seen form the table given below.

TABLE I.

Time	0	$l-x$	l	$l+x$	$2l$
Time × Velocity	0	$+$ $(l-x)\times \mathrm{PM}$	$+$ $x\times \mathrm{PN}$	$+$ $x\times \mathrm{PN}$	$+$ $(l-x)\times \mathrm{PM}$

From simple geometry it is evident from the velocity diagram that

$$\frac{\mathrm{PM}}{\mathrm{PN}}=\frac{x}{l-x}.$$

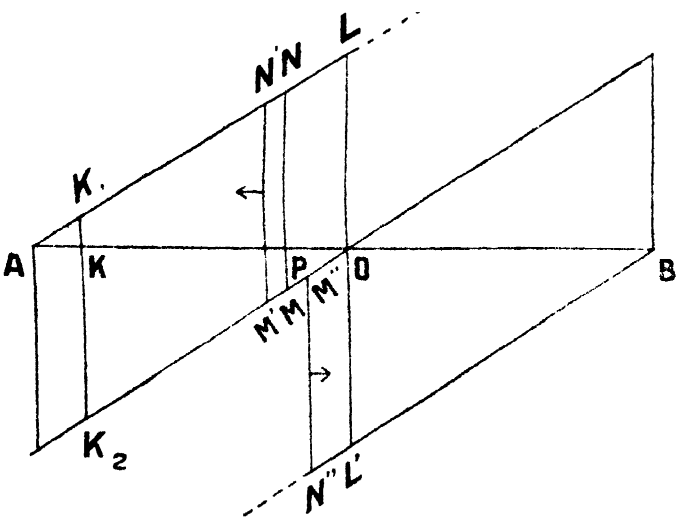
Thus

$$PM\times(l-x)=PN\times x.$$

The graph, if plotted, will be the well-known two-step zig-zag.

The second type of vibration has two discontinuites in the velocity-diagram. Its velocity-diagram is shown in Fig. II.

FIG. II



The diagram consists of three parallel lines, two passing through the two ends A and B and the third passing through the centre O of the string. Two discontinuities are supposed to be travelling in opposite directions along the length of the string. They may coincide at any arbitrary point on the string. If they happen to cross at the centre of string, the string will vibrate in two segments with the centre at rest. The vibration of each segment will be opposite to one another and the frequency of the string will be doubled. The velocity-diagram of the two halves of the string will then be like that of the first type and the vibration curve at any point will be a simple two-step zig-zag. If the discontinuities cross one another at any point P, distant x from the centre O of the string, they will again meet each other after half a period at an equidistant point Q on the other side of the centre. The curve traced by the point P at which the two discontinuities meet, may be determined as before. To begin with, one discontinuity $N'M'$ will proceed towards A and the other $N''M''$ towards B. The velocity-diagram will then be the line $AN'M'M''N''B$ and the point P will have a velocity V_2 represented by the ordinate PM. It will continue to have this velocity till the discontinuity $N'M'$ after being reflected from A crosses the point P in the opposite direction, *i.e.*, goes towards B. The velocity-diagram will then change and the point P will have a velocity V_1 given by the ordinate PN and will continue to have this velocity V_1 till the two discontinuities again meet at Q after half a period. The motion of P will be exactly reversed in the next half period. For the vibration graph of the point P, the absciassae and the ordinates are put down in the table below.

TABLE II.

Time.	0	$l-2x$	l	$l+2x$	$2l$
Time × Velocity	0	$+$ $(l-2x)\times PM$	$+$ $2x\times PN$	$+$ $2x\times PN$	$+$ $(l-2x)\times PM$

The curve, if plotted, will be the well-known two-step zig-zag. From the velocity diagram it is clear that

$$\frac{\mathrm{PN}}{\mathrm{PM}}=\frac{\mathrm{V}_1}{\mathrm{V}_2}=\frac{l/_2-x}{x}$$

Thus it is seen that the point P alternates between two velocities V_1 and V_2 which are related to one another as its distances from the centre and one end of the string. Similarly the motion of the point O, the centre of the string and of any point K distant x from the end of the string can be determined as before. The abscissae and the ordinates of the respective points are given below.

TABLE III.

For O, the centre of the string.

Time.	0	x	$l-x$	l	$l+x$	$2l-x$	$2l$
Time × Velocity.	0	$+$ $x\times \mathrm{OL}'$	$+$ 0	$+$ $x\times \mathrm{OL}$	$+$ $x\times \mathrm{OL}$	$+$ 0	$+$ $x\times \mathrm{OL}'$

The centre being first displaced to one side remains at rest for a long time and is then carried on to the other side where it remains at rest for a long time. This explains the fact that the string is seen apparently in two positions of rest at the centre, when the string is bowed at some point away from the centre. The graph, if plotted, will be one with two horizontal steps.

TABLE IV.

For the point K, distant x from the point A.

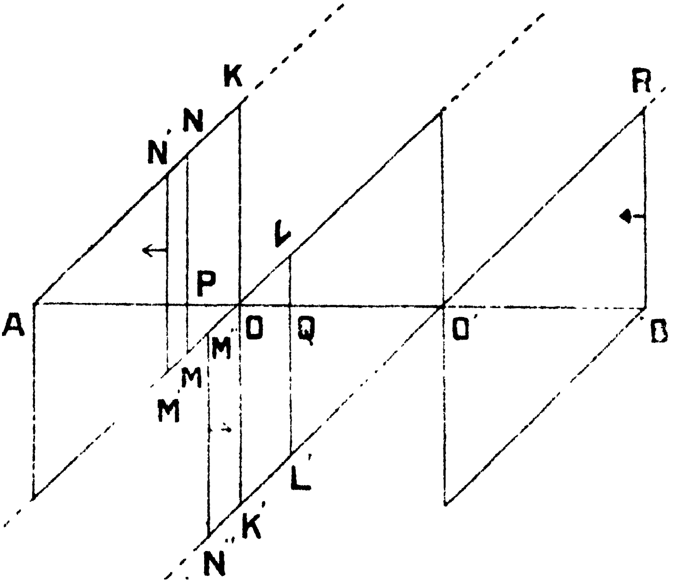
Time	0	$l/2-2x$	$l/2$	l	$3l/2$	$3l/2+2x$	$2l$
Time × Velocity.	0	$+$ $(l/2-2x)\times \mathrm{KK}_1$	$+$ $2x\times \mathrm{KK}_2$	$+$ $l/2\times \mathrm{KK}_1$	$+$ $l/2\times \mathrm{KK}_1$	$+$ $2x\times \mathrm{KK}_2$	$+$ $(l/2-2x)\times \mathrm{KK}_1$

From the geometry of the velocity-diagram it is evident

$$\frac{KK_1}{KK_2}=\frac{x}{l/2-x}.$$

The curve, if plotted, will be a four-step zig-zag. The point K will alternate between two constant velocities represented by KK_1 and KK_2 four times during each period.

FIG. III



The above figure shows the velocity-diagram of the vibrations of the third type. It consists of four parallel lines of which two pass through the two ends A and B of the string and the other two pass through the points of trisection O and O′ of the string. Three discontinuities N′M′, N″M″ and BR travel along the string as shown by the arrow heads in the diagram. Let P be the point where the two discontinuities N′M′ and N″M″ coincide, when the third discontinuity is at the end B of the string. Then, as before, by considering the changes of velocity due to the movement of the discontinuities, the vibration-curve at any point can be found in precisely the same way as before. If the length of the string be l and OP and OQ be equal to $2x$ and x respectively, the vibrational forms of the point O, the point of trisection of the string, of P, the point from where equal and opposite coincident discontinuities start, and of Q, the point where also the discontinuities M′N′ and BR cross after one reflexion of the former, can be obtained from the following data.

TABLE V.

For O, the point of trisection of string.

Time	0	$2x$	$2l/3-2x$	$2l/3$	l	$4l/3$	$4l/3+2x$	$6l/3-2x$	$2l$
Time × Velocity.	0	+ $2x \times OK'$	+ 0	+ $2x \times OK$	+ 0	+ 0	+ $2x \times OK$	+ 0	+ $2x \times OK'$

The graph, if plotted, will exhibit three horizontal steps.

TABLE VI.

For P, from where the two coincident discontinuities start.

Time	0	$2l/3-4x$	$2l/3+2x$	l	$4l/3-2x$	$4l/3+4x$	$2l$
Time × Velocity	0	+ $(2l/3-4x) \times PM$	+ $6x \times PN$	+ $(l/3-2x) \times PM$	+ $(l/3-2x) \times PM$	+ $6x \times PN$	+ $(2l/3-4x) \times PM$

From the geometry of the velocity-diagram it is evident

$$\frac{PN}{PM} = \frac{l/3-2x}{2x}.$$

The graph, if plotted, will be a four-step zig-zag curve.

TABLE VII.

For Q, where also the discontinuities cross.

Time	0	$3x$	l	$2l-3x$	$2l$
Time × Velocity	0	+ $3x \times QL'$	+ $(l-3x) \times QL$	+ $(l-3x) \times QL$	+ $3x \times QL'$

From geometry it appears that

$$\frac{QL}{QL^1}=\frac{x}{l/3-x}.$$

The motion at Q is representable by a two-step zig-zag, and Q therefore corresponds to the bowed point.

Similarly, vibration graphs of different points may be obtained, when the two coincident discontinuities start from a point distant $2x$ from O, remote from P.

3. *Experimental Method.*

The apparatus used in the experiment consists of a hollow wooden box with a groove cut in front of it. Within the groove moves a metal plate with a fine slit cut on it. A meter scale is fixed to the box immediately above the groove. The string is fixed in front of the groove and passes over two bridges fixed at the two ends of the meter scale. The vibration of any point of the string is recorded by bringing the slit opposite to the required point and receiving the shadow of the string across the slit on a photographic paper contained in a dark-slide which slides within the wooden box parallel to the string. The necessary illumination is provided by an arc lamp placed in front of the apparatus. The motion of the bow is recorded by sticking a number of pins at right angles to the rod of the bow and receiving the shadow of these pins moving with the same velocity as the bow, on the photographic paper along with the shadow of the string. The ratio of the velocities of the two components of the zig-zag curve is determined with a finely divided cross-section paper and a long narrow smooth glass plate with a fine line etched on it. The section paper is fixed to the drawing board and the photographic record of the vibration curve is fixed on it, taking care that a horizontal line on the section-paper passes through all the tips of the zig-zag curve. One vertical line and one horizontal line of the section-paper are taken as axes. The tangent of the inclination of each step is obtained by putting the etched line parallel to the edge of the step and taking the ratio of the intercepts on the vertical and horizontal line of the cross-section paper, referred to as axes. For each determination of the value of any tangent, nine or ten readings are taken and the mean value is used. Similarly for determining the velocity of the bow, the tangent of the inclination of the photographed line of the pin attached to the bow on the vibration record is taken. The ratio of the velocity of the bow to that of the string is determined as before with a fine etched line on a glass plate and a finely-divided cross-section paper.

4. *Verification of Generalised Law.*

The equation $\frac{V_1}{V_2}=\frac{x}{l \quad -}$ holds in the vibration of the *n*th type, where

V_1 = Velocity of ascent of the bowed point
V_2 = Velocity of descent of the bowed point
x = Distance of the point from the nearest node of the *n*th harmonic
l = Length of string
n = Any integral number.

In the case of the second type of vibration $n=2$, the equation is reduced to $\frac{V_1}{V_2}=\frac{x}{\frac{l}{2}-x}$. To get the second type of vibration, the string is bowed at different distances from the centre of the string. The point on an equal distance from the centre of the string on the opposite side is observed. The vibration curve at this point is always found to be a two-step zig-zag.

Calling V_1 and V_2 the respective velocities of the two steps of the zig-zag curve, the ratio $\frac{V_1}{V_2}$ has been put down in the table given below.

TABLE VIII.

Bowed Region.	Observed point.	Mean V_1	Mean V_2	Observed $\frac{V_1}{V_2}$	Calculated $\frac{V_1}{V_2}$	x	$\frac{l}{2}$
51·6—52·4	48	5·86	·241	24·3	25	2 c.m.	50 c.m.
52·6—53·4	47	4·61	·263	17·4	16·7	3 ,,	,,
53·6—54·4	46	2·98	·256	11·6	12·5	4 ,,	,,
54·6—55·4	45	2·64	·249	10·6	10	5 ,,	,,
55·6—56·4	44	1·88	·248	7·4	8·3	6 ,,	,,
56·6—57·4	43	1·77	·243	7·3	7·2	7 ,,	,,
57·6—58·4	42	1·71	·293	5·8	6·2	8 ,,	,,

In the third type of vibration $n=3$ and the equation becomes $\frac{V_1}{V_2}=\frac{x}{\frac{l}{3}-x}$. The string is bowed at different distances from one of the points of tri-sections of the string and the ratio of $\frac{V_1}{V_2}$ is tabled below.

TABLE IX.

Bowed Region.	Observed point.	Mean V_1	Mean V_2	Observed $\frac{V_1}{V_2}$	Calculated $\frac{V_1}{V_2}$	x	$\frac{l}{3}$
63·2—64	36·8	3·22	·298	10·8	11·1	3 c.m.	33·34
64·2—65	35·3	5·92	·357	16·5	16·7	2 ,,	,,
68·2—69	31·3	3·82	·238	16	16·7	2 ,,	,,
69·2—70	30·3	3·24	·284	11·4	11·1	3 ,,	,,

From the above it is clear that the generalised law of the vibration of bowed strings agrees with facts, the observed value of $\frac{V_2}{V_1}$ being the same as the calculated values within the limits of experimental error.

5. *The Relation of Bow Velocity to String Vibration.*

The string is bowed at 1/8th and 1/7th of its length and four points, two ahead and two behind the bowed region, are observed. The ratio of the velocity of the string to that of the bow is found in the manner described before. The results are shown below.

TABLE X.

The length of the string = 100 c.m.

Bowed region 12·1 to 12·9. c.m.

Points of Observation.		10·5	11·5	13·5	14·5
Mean $\frac{V_S}{V_B}$	Bowing Quick	·821	·915	1·110	1·121
	„ Moderate	·848	·923	1·080	1·124
	„ Slow	·827	·975	1·026	1·104

TABLE XI.

The length of the string 100 c.m.

Bowed region 14 to 14 8.

Points of observation.		12·5	13·5	15·3	16·3
Mean $\frac{V_S}{V_B}$	Bowing Quick	·818	·939	1·014	1·114
	,, Moderate	·875	·891	1·029	1·090
	,, Slow	·837	·912	1·071	1·117

TABLE XII.

The length of the string 50 c.m.

Bowed region 42·5 to 43·3 c.m.

	Points of observation	40·9	41·9	43·7	44·7
Mean $\frac{V_s}{V_B}$	Light pressure and slow bowing	1·194	1·076	·768	·685
	Hard pressure and slow bowing	1·208	1·031	·821	·693
	Light pressure and quick bowing	1·256	1·083	·740	·638
	Hard pressure and quick bowing	1·801	1·104	·800	·649

The data were plotted with $\frac{V_s}{V_B}$ (ratio of the speed of the string to that of the bow) as ordinate and the position of the observed point on the string as abscissa. In each case, see for instance Fig. IV, the point on the string having the same velocity as that of the bow has always been found to lie within the bowed region. It never goes away from the bowed region in the manner suggested by K. C. Kar.[1] In case of a string of short length (say 50 c. m.) the zero point is sometimes found to go ahead of the outward limit of the bowed region by 1 or 2 mm. This deviation may be due to the errors of the experiment, as with the shorter lengths of the string the measurements are less precise. It has been found that the variation of bowing pressure and change in the velocity of bowing have little effect on the relative values of the velocity of the string and that of the bow. The ratio of the two remains practically the same. It has been found that the velocity of any forward point, that is, the point lying outside the bowed region has always a greater velocity than that of the bow whatever may be the bowing pressure and the velocity of bowing. A good number of photographs had been taken with different bowing pressures and with different velocities of bowing. In not a single one of them was the bow line found to be parallel with the string line in the manner claimed to have been found by Kar.

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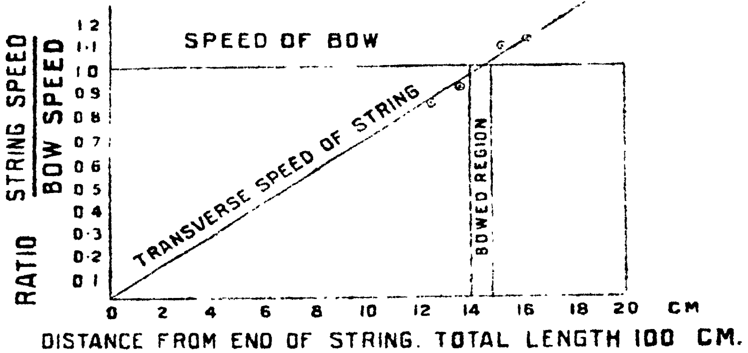
[1] K. C. Kar. Physical Review, Vol. 20, 1922, p. 148.

FIG. 4



6. *Transitional Forms of Vibration.*

When the bow is applied at a point of aliquot division of the string, all the harmonies having a node at such a point are absent in the motion maintained by the bow. For example, when the bow is applied at $\frac{l}{5}$, the fifth, the tenth, the fifteenth, etc., harmonics will be missing in the vibration of the bowed point. Similarly the sixth, the twelfth, etc., harmonics will drop out, in case the point distant $\frac{1}{6}$ from the end of the string is bowed. The vibration-forms at the bowed point in the above cases will be a two-step zig-zag, the velocities of its two components being inversely as the distances of the bowed point from the two ends of the string. When the bow is gradually removed from $\frac{l}{5}$ to $\frac{l}{6}$, the fifth, the tenth harmonics, etc., gradually reappear and the sixth, the twelfth harmonics, etc., become feebler and feebler and finally disappear. In these intermediate cases the forms of vibration are not exactly of the Helmholtzian type, but they are modified to some extent. Raman[1] has mathematically analysed these vibrations and traced the changes in the character of the vibrations in the course of the passage of the bow from one node to the next node. The forward motion of the bowed point is uniform and has got a velocity equal to that of the bow, and the backward motion is not uniform. But it is well known that the tones elicited by bowing depend on the position of the bowed point, the bowing pressure, the velocity of bowing, etc. An attempt has been made to get approximately the Helmholtzian type of vibration by bowing at different points lying between two consecutive nodes, with different bowing pressures and different speeds of bowing. For, the steady vibrations of the string excited by the bow, which are of musical interest, have approximately the characters of the simple Helmholtzian type.

A string, 100 c.m. long, is bowed at different points at an interval of 1 c.m. between 75 c.m. and 86 c.m., and the corresponding points on the other side of the string are observed. The results of observation are put down in the table below. v_1 and v_2, as before, represent the respective velocities of the steps of the two-step zig-zag curve.

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[1] C. V. Raman, Phil. Mag. Vol. 38, Page 578, 1919.

TABLE XII(*b*).

The length of the string = 100 cm.

Bowed Region.	Observed point.	Mean V_1	Mean V_2	$\frac{V_1}{V_2}$	Helmholtzian values of $\frac{V_1}{V_2}$	REMARKS.
74·6—75·4	25	·93	·292	3·18	3·00	
95·6—76·4	24	1·02	·304	3·36	3·17	
76·6—77·4	23	1·96	·298	6·6	3·35	$\frac{V_1}{V_2}$ for the 5th type of vibration = 6·6.
77·6—78·4	22	1·60	·200	8	3·55	$\frac{V_1}{V_2}$ for the 4th type of vibration = 8·3.
78·6—79·4	21	1·04	·244	4·26	3·76	
79·6—80·4	20	1·49	·354	4·2	4·00	
80·6—81·4	19	1·02	·210	4·9	4·26	
81·4—82·2	18·2	2·04	·205	9·9	4·49	$\frac{V_1}{V_2}$ for the 5th or the 6th type of vibration = 11·1.
82·9—83·7	16·7	1·82	·368	4·9	5·00	
84·2—85	15·4	1·45	·260	5·6	5·49	
85·3—86·1	14·3	2·78	·463	6	6·00	

It appears from the above observations that when a string is bowed with suitable pressure at any arbitrary point between one-fourth of the length of the string and the end of the string, the Helmholtzian relation is in general approximately satisfied. But when the bow is applied at a nodal point such as $\frac{2l}{9}$ or thereabouts, the value of $\frac{V_1}{V_2}$ rises and attains the values for the fifth or the fourth type of vibration. The same thing takes place, when the nodal point $\frac{21}{11}$ is bowed, the value in this case corresponding to that for the fifth or the sixth type of vibration.

SUMMARY.

1. The vibration form of a string is very simple, when it is bowed near an end but becomes more complicated when bowed far from the end. These different modes of vibrations have been classified by Raman according to the number of discontinuities on the velocity-diagram. The vibration with one discontinuity is termed the vibration of the first type and the vibration with two discontinuities is termed the vibration of the second type and so on. The velocities of ascent and descent of a bowed point in the *n*th type of vibration are given by the equation $\frac{V_1}{V_2} = \frac{x}{\text{[illegible]}}$, where V_1 and V_2 are the velocities of ascent and descent, and x, the distance of the bowed point from the nearest node of the *n*th harmonic and l, the length of string. Vibrations of the second type are obtained when the string is bowed at different distances from the centre of the string; the corresponding points on the other side of the centre may be conveniently observed. Similarly, for vibrations of the third type, different points lying on either side of a point of tri-section of the string are bowed and corresponding points on either side of the other point of the point of tri-section of the string may be observed.

2. The generalised law of the bowed string given by Raman has been experimentally verified with the help of the vibroscope, the photographs being measured with a finely divided cross-section paper and a fine line etched on a glass plate. The velocities of ascent and descent of a bowed point are measured by determining the slope of the lines in the vibration-curves.

3. A number of pins stuck at right angles to the bow enables the velocity of the bow to be determined in the same way by the measurement of the slope of the photographic record of the motion of pins. Two points lying ahead of and

two points lying behind the bowed region are observed in each case. Graphs have been drawn with the ratios of the velocities of the string to those of the bows as ordinates and the lengths of the string as abscissae. A point lying ahead of the bowed region is always found to have a velocity greater than that of the bow and a point lying behind the bowed region is always found to have a velocity less than that of the bow. The point having the same velocity as that of the bow is always found to lie within the bowed region and does not deviate therefrom in the manner suggested by K. C. Kar.

4. Steady vibrations of the string maintained by the bow, which are of musical interest, have got approximately the characteristics of the simple Helmholtzian relation. As the character of the notes, elicited by the bow, depends on the position of the bowed point, the pressure of bowing, the speed of bowing etc., an attempt has been made to get the Helmholtzian type of vibration by bowing different points, between one-fourth the length of the string and the end of the string with suitable pressure. A string 100 c.m. long, is taken and points, at an interval of 1 c.m. between 74 c.m. and the end of the string, are bowed and the ratios of $\frac{V_1}{V_2}$ of the vibration curves of these points are calculated. It is observed that the Helmholtzian relation holds approximately in all cases except at the nodal points such as $\frac{2l}{9}$ or $\frac{2l}{11}$ or thereabouts. The values of $\frac{V_1}{V_2}$ then rise to those for the fourth, fifth, or sixth type of vibration as the case may be.

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Experimental Study of the Laminar Motion of a Viscous Liquid.

By

BORIS WEINBERG.

(PLATES XII AND XIII)

1. *"Solid" and "Liquid."*

The previous two articles in this journal[1] dealing principally with the transformations of *solids* as well as the present one devoted to the motion of *liquids*, oblige me to definitely state the meaning I attribute to their notions. I always insisted[2] on the solids, liquids and gases being not *classes* of material bodies but merely types of solids and I defined solids as bodies displaying considerable forces in case their form or volume were changed; liquids as bodies displaying considerable forces in case of changes of their volume and negligible ones as regards the changes of their form; gases as bodies displaying negligible forces as well for changes of their form as of their volume. Such an understanding being sufficient for physics and coinciding with the sense which is attributed to these notions in practical life shows clearly that except *typical* solids, liquids and gases, there may be all sorts of *intermediate* bodies.[1] Therefore a classification—if any be generally possible—may depend only on very arbitrarily and quite conventionally stated limits for the constants characterizing the resistivity of the material of a body to the changes of the form—N (modulus of rigidity) and η (co-efficient of internal friction) and of the volume—γ (co-efficient of compression). From this standpoint I opposed (7) to the tendency to substitute the identification of the notions "solid" and "crystalline" to such an understanding of the notion of solid and indicated as argument against this statement (*30*) that even such a defender of the identity of the solid and the crystalline state as Tammann having in his hand a glass-bottle with oleate of ammonium would not call the recipient liquid and its contents solid although from the standpoint "amorphous-crystalline" glass is an over-cooled amorphous liquid and oleate of ammonium—a liquid crystal.

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[1] Proc. Ind. Ass. Cult. Science 9,215-250, 1926 and Ind. Journ. Phys., Vol. I, 279—310, 1927. These two papers shall be cited further under the NN 53 and 54, the numbers 1-52 relating to the papers enumerated in the first one (53,247-250).

[2] From my first scientific-popular paper in 1890 but especially in my general treatise on physics (2 parts 1908-10) and in my report on the successes of the physics of solids read to the II Mendeleev's Congress of 1912 (30).

The resistivity of a body to the action of external forces depends not only upon the values of N, η and γ but also upon the limits of elasticity and of plasticity relating to changes of the form and volume.[2] Therefore a typical solid is a body the material of which possesses a sufficiently high limit of elasticity δ for shear *or* a very high co-efficient of internal friction η, and a typical liquid—a body the material of which has a very low δ and a not too great η. Pitch at ordinary temperatures is in this *quantitative* sense a typical solid, although it has a fairly small δ.

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[1] As an illustration I have had for my lectures a collection of bottles with different solutions of dammar-resin in turpentine oil, possessing gradually increasing values of η (*54*).

[2] The number of *independent* limits of elasticity and plasticity for various types of deformation which I have previously considered equal to 4 (*30*) must be reduced—as I think now (*40, 41*)—to 3, namely (1) a limit of elasticity, (2) a limit of plasticity relating to gradually increasing tangential stresses which tend to change the *form* of a body and (3) a limit of plasticity for negative pressures. The limit of elasticity for negative pressures must coincide with the limit of plasticity because no residual diminutions of density are possible if even we could subject a body to a *uniform* omnilateral extension. For positive pressures, seems to exist neither a limit of elasticity nor of plasticity, although *Kock's* experiments on the breaking in pieces of rock salt crystal after its omnilateral compression (Diagl. Journ., *274*, 405-409, *1889*) can be considered as an argument against the above statement.

But *qualitatively* the transformations of the " solids " which have a very small δ are quite analogous to the so—called laminar motion of typical liquids which can be observed more or less easily only on sufficiently *viscous* liquids—in liquids with a rather high η. That was the reason why in studying the slow deformations of *solids* and wishing to possibly shorten the duration of experiments, I unperceivably came to the experimental study of typical viscous liquids. The results of this study having an independent interest on account of reasons stated below, I shall treat here conjointly the results of the study of the " liquids " with a rather high—for a typical " liquid "—value of η as well as these of the study of solids with a rather low—for a typical " solid "—value of η and for the sake of brevity shall call both " viscous liquids."

2. *The importance of the problem of studying the laminar motion of a viscous liquid.*

Laminar motion may be defined as a motion in which no trajectory of a separate particle intersects itself or any trajectory of another particle. The contrary is the *turbulent* motion in which all the trajectories or a part of same intersect themselves or some others. The strict mechanics of the turbulent motion being unknown, the turbulence is regarded usually as a co-existence of regular vortices, regularly distributed in space (*Prandtl*, *Karman*, *Joukowsky* and other authors) or as a co-existence in different parts of the volume of the liquid separated by " surfaces of disconuity " of irregular motions of the liquid. For the sake of brevity let us call such parts, " turbulosities " The first standpoint postulates regular periodicity in the generation of the vortices, the second one does not pose this condition and has a more or less statistical character.[1] The second standpoint is more general and finds confirmations in the experimental investigations tending to disclose the exact mechanism and the inner structure of turbulent motion in some of the simplest cases.[2]

A given flow of liquid may be defined by a combination of geometric, kinematic and kinetic characteristics, *i.e.*, by the form and dimensions of the boundaries of the flowing liquid, by the trajectories of its particles and by the forces which are causing the motion of the liquid or are caused by it. *Reynolds* has shown that the character of the motion of a liquid—laminar or turbulent—for given geometric conditions of its flow and for geometrically similar flows depends on the value of a certain nondimensional quantity.

$$R \quad \frac{V\delta l}{\eta} \tag{1}$$

which is now called the "*number of Reynolds*" and in which V is the standard velocity (usually the mean) of the flow, l—the standard linear dimensions of the flow, δ the density of the liquid and η its co-efficient of internal friction.

When in increasing the velocities of the flow and consequently the standard velocity V and the value of R—we come to a certain definite value R_1 (called, "the first critical value of the number of *Reynolds*") the motion ceases to be continuously laminar: from time to time in some places of the liquid are generated separate regular vortices or irregular turbulosities which move in the liquid and gradually subside. The further increase of R increases the frequency of generation of separate turbulosities in diminishing their lability and when R attains a certain definite value R_2 (called "the second critical value of the number of *Reynolds*") a certain part of the volume of the liquid is fully occupied by turbulosites continuously generating, moving and subsiding.

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[1] *Cf. Karman.* Zeits, f. angew. Math. u. Mech., 1, p. 250. 1921.

[2] *e.g., J. N. Burgers* "Experiments on the Fluctuations of the velocity in a current of air" Proc. Amst. Acad., *19*, 547-558, 1926.

The experimental arrangements needed to follow the trajectories of liquid particles or the fluctuations of the value and the direction of the velocity in a definite point, are rather complicated. Therefore the usual method of determining the moment of attainment of R_1 and R_2, that is of transition from the strictly laminar motion to the labil-turbulent one and from the labil-turbulent motion to the stabil-turbulent one consists in the study of the relation between the standard velocity V (or the mean velocity $\bar{V}$) and the *resistance*. This resistance may be the force experienced by a solid inserted in the moving liquid or the stress experienced by the walls of its recipient or the pressure causing the flow of the liquid. For *typical* laminar motion—when R is sensibly less than R_1—this resistance is proportional to the first power of $\bar{V}$ for *typical* turbulent motion when R is sensibly greater than R_2—this resistance is proportional to the second power of $\bar{V}$.

The transition from the proportionality to $\bar{V}$ to the intermediate stage of the labil-turbulent motion for which many authors were trying to use the expression $a\bar{V}^n$ where n lies between 1 and 2 for the resistance and from this intermediate stage to the proportionality to $\bar{V}^2$ must be continuous and therefore the rigorous determination of R_1 and R_2 is as illusory as the determination of the "limit of proportional elasticity" from which start the deviations from *Hooke's* law *(30)*.

M. A. Velikanov[1]—in generalizing the *Navier-Stokes* differential equations of motion of a viscous liquid reduces them to an abridged form

$$S = \alpha R^2 + \beta R \qquad (2)$$

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[1] "The Generalised Problem of Stationary Motion"—Journ. Scient. Inst. of Amelior. (Tzvestija Nauchy Melioracionnogo Institnta), *14*,78-117. 1926 (Russ.) with an Engl resume.

where S is a dimensionless number expressing the resistance in special units and α and β are co-efficients which probably depend only on the geometrical characteristics of the flow and are identical for geometrically similar flows. If the validity of this assertion be ultimately proved, every motion must be regarded as being at the same time laminar and turbulent. But for small values of R, S must be practically independent of the first member of the expression (2) (*linear* hydrodynamics as it is named by *Velikanov*, *i.e.*, the motion must be *typically* laminar and the probability of generation of a turbulosity must be practically excluded; and for great values of R, S must be practically independent of the second member of the expression (2) (*quadratic* hydrodynamics according to *Velikanov*), *i.e.*, the motion must be *typically* turbulent, the probability of existence of spaces unoccupied by turbulosities must be practically excluded. The laminar and turbulent motions are thus no distinct *classes* of phenomena in liquids but just well propounced *types*.

The expression (2) shows by-the-bye the futility of the attempts to use the formulæ of the type aV^n for the intermediate stage.

It is interesting to note that the quadratic hydrodynamics is practically independent of η—a circumstance justifying the historical development of hydrodynamics of "ideal" liquids possessing $\eta = o$—a case which from the physical standpoint is an absurdity.

For different geometrical characteristics of flows the values of R—and consequently of R_1 and R_2—are not comparable on account of indeterminateness of what must be taken for the standard velocity V and still more for the standard linear dimension l. For instance in the case of a falling sphere, V is taken as the velocity of the sphere itself although this velocity is *maximal* and in the case of the motion of liquid through a cylindrical tube—the *average* velocity but not the velocity along the axis which is maximal. In both cases for l is taken the *radius* (of the sphere or of the cylinder) but in the case of longitudinal motion of a liquid between two coaxial cylindrical surfaces—the *difference* of their radii.

It is therefore highly desirable to cancel this indeterminateness and to find a purely physical criterion which should allow to compare flows of different geometrical conditions. It seems to me that the way to such a criterion consists in attempts to replace the number R (1) which characterizes the whole of the flow by some other non-dimensional number N which would characterize each separate point of the flow. The form of participation of δ and η in the expression of type (1) being beyond any doubts, it is the indeterminate expression Vl which has to be replaced by an expression relating to an individual point. *Pour préciser les idees,* let us assume that N is the sectorial velocity taken relatively to some point of the boundary of the flow. Then if *for every* point of the flow N would be less than a certain critical value N_1 the motion would be typically laminar but if in increasing all the velocities we should attain that in a certain part of the volume the values of N would exceed N_1 the geometrical place of the points where $N=N_1$ would separate the "*laminar layer*" where the motion would continue to be laminar from the space where the motion became labil-turbulent.[1] At still greater velocities in a part of the volume N becomes greater than N_2 and the geometrical place of the points where $N=N_2$ separates the "*turbulent layer*" where the motion should continue to be labil-turbulent from the space where the motion would be stabil-turbulent. Such a standpoint coincides with the results of several experimental researches of different authors.

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[1] An interesting example of theoretical determination of the thickness of such a boundary layer in the case of an infinitely broad flow of constant height based on the calculation at which *distance l from the bottom* the number of *Reynolds* attains the value R, is given by *M. A. Velikanov* in his article "On the boundary velocity of a turbulent flow"—Journ. Russ. Phys. Soc., 57, 113-117, 1925 (Russ.).

Now if we were to postulate the necessity of taking into account some kind of a *local* characteristic N or if we found it possible to compute as it was done by *Velikanov* (l.c.) the number of *Reynolds* for a separate vortex, whirl, eddy or turbulosity the motion of the liquid in each whirl or turbulosity ought to be rigorously laminar. Indeed if the standard velocity V in this whirl would be too great for its standard transverse dimension l, the number of *Reynolds* would exceed the critical value R_1 for it and the whirl would generate several smaller "whirlets" in which the motion either would be laminar or which at their turn would generate still smaller whirlets.

From this standpoint even every typically turbulent flow consists of a finite number of finite component parts in each of which the motion is laminar and has in the neighbourhood of its solid boundaries laminar boundary layers which at measure of diminution of the value of R tend to grow and finally fill up all the space of the flow making it typically laminar.

All such considerations show the importance of studying critically (*39*, *46*, *48*, *49*,) as well as experimentally the laminar motion. The importance of such a study which I have pointed out many years ago (*12*, *16*, *18*) is increased by the fact that for many metals the deformations beyond the limit of elasticity consist in mutual displacements of their crystallites which must be accompanied by *laminar* motions in the less viscous matter filling the interstices between their boundaries. This order of ideas (*34*) led me to investigate the influence of admixtures of indifferent solid particles (sand, seeds of turnip—"natural shot") to liquids of different initial viscosity η_0 and has shown me that for practically similar form of the admixed solid particles the quotient of η to η_0 is independent of η_0 (for η_0's within 0·01 to 10 *c. g. s.*) and can be expressed (for spherical particles) by the formula

$$\frac{\eta}{\eta_0} = 1 + 0{\cdot}3\, v^2 \qquad \ldots \quad (3)$$

where v is the volume percentage of the neutral admixture. This can be seen from Table I.

TABLE I.

	v =	10	20	30	40	15	60	55
$\frac{\eta}{\eta_r}$	abs.	1·2	1·9	3·5	5·7	7·0	8·7	11·8
	calc.	1·3	2·2	3·7	5·8	7·1	8·5	(10·1)

3. *Choice and preparation of liquids.*

The co-efficient of internal friction for usual liquids being small, those who were studying the laminar motion had to recur to rather restricted dimensions of the bore of the tube or of the diameter of the balls falling through the liquid.

If however we take liquids with a sufficiently high η we can considerably augment the dimensions without risking to approach the turbulent motion and can thereby obtain more detailed experimental data on the laminar motion. This order of ideas suggested me to undertake several investigations some of which give rather satisfactory results—at least what concerns methodology.

One of the principal conditions of success is evidently the choice of a suitable liquid. It must satisfy the following requirements :

1. It may be prepared or acquired in large quantities and be homogeneous.
2. It must not be expensive.
3. The co-efficient of internal friction may be varied within wide limits.
4. It must be sufficiently transparent.

The last requirement is not indispensable and for instance the mixtures of pitch with petroleum proposed and used by *Kuznecov* (*28*) are quite satisfactory in many cases.

The condition of transparency is satisfied by mixtures of turpentine-oil with colophonium (sort WW = water white) and with dammar-resin. The latter are very expensive but very transparent for visible rays (although not for ultraviolet radiations). As regards viscosity, it is easy to prepare —*cf.* *54*,—a solution of any desired value of η up to 10^9.

For preparing such mixtures in large quantities (as well as for melting at once and cautiously) considerable masses of asphalt, pitch, etc., we finally adopted (*32*) an apparatus which is represented in fig. 1 and was substantially a heating bath with machine oil. When the temperature of the oil was 170-180° C., the substances to be melted or mixed were put in the inner vessel, the latter was covered with its lid and the water was set into the refrigerator in order to return the volatile components back into the inner vessel. When the solid components were softened, the stirrup was put in action and in 1-2 hours after the beginning of the operation the liquid was ready and could be poured where necessary. For the sake of security the lid of the oil-bath was provided with a thermo-regulator and also with a refrigerator.

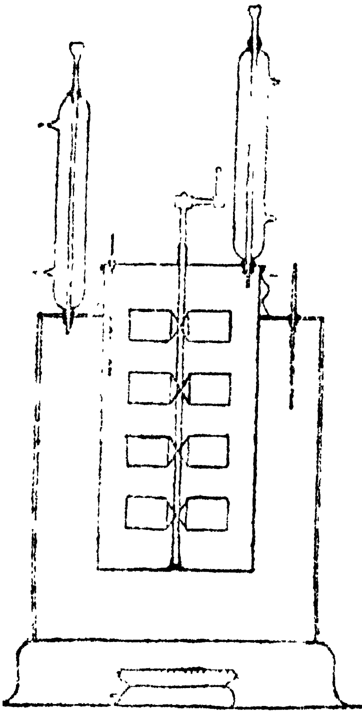

Fig. 1.

Using such precautions we could obtain considerable portions—up to 25—30 kg's at once—of a liquid rather uniform, a condition which has been necessary in some experiments. For smaller quantities we had a similar apparatus having the refrigerator in the form of a metallic worm inserted in the lid of the inner vessel.

4. *Study of the kinematic conditions of laminar motion.*

The investigations of laminar motion comprise two kinds of questions—questions relating to kinematics of the motion and those relating to its kinetics. Regarding the kinematics, the most essential should be the possibility of pursuing the displacements of a liquid particle—of a very small element of the volume of the liquid. The laminar motion being usually very slow it is probable that any means proper for a direct determination of the *velocity* at a certain point of a liquid—*e.g.*, the *Pitot's* tube—are not appliable here. Some data on the distribution of the velocity can be obtained by means of the measurement of the quantities of liquid flowing through certain sections.

Regarding the trajectories of liquid particles, all the elements of a liquid being identical, we have to use special indicators of the displacements of an element of a liquid. Let us consider successively the indicators (*a*) of the element located at the free surface of a liquid, (*b*) of the element located in the interior of a liquid in the case when there exist differences of pressures and (*c*) of the element located in the interior of a liquid in the case when there are only tangential stresses.

(*a*) *Indicators of displacements of the elements of a liquid located at the free surface of a liquid.* Every body of sufficiently small dimensions and of a density inferior to the density of the liquid can serve as such an indicator. For very viscous liquid the question of smaller density is not indispensable because even heavy small bodies sink very slowly in such liquids.

For pitch, I obtained (*13*) enough satisfactory results making on its surface narrow stripes with oil-paint: although such a point was diffusing a little in the pitch still during several days the lines were narrow enough as can be seen from fig. 2. (Plate XII). This figure is a photograph of three gutters of a uniform section (a half of a square ⊔ divided parallelly to one of its sides—to the left, a half of a square ∨ divided along the diagonal—in the middle; the section of the Hintereisferner—to the right). These three gutters were filled with pitch, on its surface were traced equidistant ($d=10$ cm.) white lines and then the gutters were inclined ($\tan \alpha=0{\cdot}30$) and photographed from time to time; fig. 2 in Plate XII represents their view after three days.

In order to avoid the expansion of the oil-paint I have tried (23) to use a glue-paint but the results were less satisfactory: the stripes did not deform in a plastic manner but broke in several rectilinear pieces, hindering thereby to make as precise measurements as with oil-paint lines.

(*b*) *Indicators of displacements of the elements of a liquid located in the interior of the liquid when there exist differences of pressure.* I have met with such a case in trying to follow the closed trajectories which must describe the particles of a viscous liquid when a solid passes through it. For this purpose I made (32) a hollow wooden cylinder ($d=14$ cm., $h=50$ cm.) divided in two parts and supplied with corresponding plates at the bases and have filled each part with pitch. On the surface of one of these two pitch-semi-cylinders were put in quadratic order small ($d=\frac{1}{8}''$) bicycle-balls, the two semicylinders were juxtaposed and the whole was put vertically after having placed a 5 cm. automobile-ball on the top of the 14 cm. pitch cylinder. The descending motion of the big ball through pitch, the moving asunder of the little ones when the big ball was approaching them, their back motion towards their former positions, were followed by means of daily Röntgen-ray photographs. But this attempt was unsuccessful: the back motion of the little balls was much smaller than their forward displacement.

The same circumstances, but still more accentuated, were met by *V. N. Alfimov* and myself when we were carrying out an analogous experiment with a mixture of turpentine-oil and dammar-resin having an η of the order of 10^4 and with small glass-balls: the big ball moved the little ones asunder only after having approached those very near.

All this has shown to us that solid indicators are useless when differences of pressure exist in the liquid: the liquid flows partly around such an indicator and its displacement is less and can have another direction than the displacement of the element of the liquid the place of which it has occupied. The difference of displacements must diminish with the diminution of the dimensions of an indicator but these dimensions cannot be diminished indefinitely, a single indicator becoming soon imperceptible. If we take no single indicators situated at perceivable distances from each other we come to the use of definite volumes—for instance of parallel layers—of a liquid of the same density and of the same viscosity but of another colour, what has been already applied in many investigations.

I shall mention also the method of *Reiger*[1] who stretched across the viscous liquid narrow and thin rubber-strips and attributed the somewhat smaller displacements of these strips in comparison with the displacements of the liquid not to the flow of the liquid around them but to their tension.

(*c*) *Indicators of displacements of the elements of a liquid located in the interior of the liquid when there are only tangential stresses.* In such cases small solid spheres of an approximately equal density would probably be adequate.

5. *Study of the kinetic conditions of laminar motion.*

The purpose of this study is to elucidate the relation between the forces acting on a liquid or on a solid moving relatively to the liquid and the velocities of the liquid or of the solid. The difficulties concerning the determination of the velocities of a liquid were discussed in the preceding paragraph. I may add that the determination of the velocity of a solid which is usually related to the walls of the recipient of the liquid is much more easy.

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[1] Ann. d Phys., *19*, 1005, 1906.

Regarding the forces we must always take care not to fall into the Scylla of turbulent motion or in the Charybdis of too small velocity and of too long duration of experiments. But there is a trusty steerman: the viscosity of the liquid, being combined with the dimensions of the recipient of the liquid and of the solids immersed in it, can always save you. The choice must however be the result of preliminary trials.

A high viscosity sets aside the danger of critical and ultracritical velocities but evokes, on the contrary, the inconvenience of too considerable forces or of too small velocities at which the influence of the uncertainty of temperature can become preponderant. A small viscosity makes the forces with which we have to deal so minute that even the force of gravity acting on the liquid becomes excessive. In the case of a solid immersed in such a liquld the smallness of the forces which act on it exaggerates the influence of pulleys, of threads which draw or retain the solid, and of other appurtenances. We could overcome these diffisulties by increasing the dimensions of the solid but then we ought to recur to an immense recipient or to exclude the influence of its walls.

The influence of the walls when the distance between those exceeds but slightly the dimensions of the solid, increases very much the resistance of the liquid to the motion of solid and ought to be the subject of special researches which may modify the form of the correction-term relating to small values of the quotient of transverse dimensions of the solid and of the recipient. Some results of such investigations (*28. 32, 37*) will be given in the § 8.

Fig. 2

Photograph of three gutters.

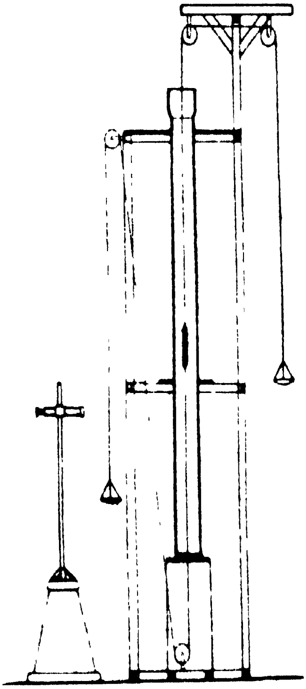

Fig. 4

6. *Some results of the study of laminar motion of a viscous liquid in the case of immovable walls or of an immovable wall and a free surface.*

We may classify different cases of motion of a liquid by using the notions of an immovable wall, of a movable wall, of a free surface and of a free wall (*46*) and understanding by "under a wall" a surface of a solid which is in contact with the liquid, and by "under a free surface" a surface of the liquid which is in contact with a gas or with another liquid, this gas or liquid exhibiting no tangential stresses on the liquid under consideration. If the wall does not act tangentially on the liquid it may be called a free wall; if the external forces acting on the wall are insufficient to hold it in rest, the wall may be called movable and in the opposite case—immovable. I may mention that in some cases the theoretical solution of the problems of motion of a liquid between two immovable walls and between one immovable and one movable, gives directly the solution of the problem concerning the motion between one immovablo and one free wall (*39*).

I. *Flow in a tube.* That is the only case of one immovable wall with no free surface (the surfaces of inlet and of outlet being of no interest—especially in the case of a flow under the action of gravity) for which we can have the stationary stage of the motion. A case of more detailed study of the steady *laminar* motion in a tube—the observations of *Gostjunin* and *LeDentu*—was considered in the previous paper. I may mention here my investigation (*47*) on the unsteady stage—on the processes of rise and descent of a viscous liquid in a capillary tube undertaken in order to give the possibility of determining the superficial tension without awaiting the asymptotically reached final height H. Theoretical deduction leads to the formula

$$h = H - (H - h_0)\, e^{-\frac{r^2 \delta g (t - t_0) + 8\eta (h - h_0)}{H + l}} \qquad (1)$$

where h and h_0 are the heights of the liquid at the moments t and t_0, r—the radius of the tube, l—its length under the free level in the vessel, δ—the density of the liquid and e, g and η have their usual meaning. The formula (4) was confirmed by measurements made by *S. M. Voinov* and *A. M. Mocalin* on solutions of dammar-resin in turpentine-oil with η of an order from 10^0 to 10^2.

II. *Flow in an inclined channel.* That is the only case of one immovable wall and of one free surface. Such a laminar motion has become the subject of studies only during last two decades.

The case of a plane, practically infinitely broad, channel was experimentally studied with liquids of low viscosity and especially for determining the value of Reynolds critical co-efficient—in 1910 by *Hopf*[1].

In 1906 in connection with my theory of glaciers (see *54*) I have enunciated a theorem which, as I found only recently (*46*), was given in 1845 by *Stokes* (Trans. Cambr. Phil. Soc., *8*, 286-319. 409-414, 1848), connecting the solution of the problem of flow of a viscous liquid in a channel with the problem of its flow in a tube obtained in covering the channel with a similar channel representing the mirror-image of the first one. In order to verify this theorem and to realize the laminar motion in an inclined channel I made numerous observations on the flow of solid pitch in gutters of different transverse sections (see fig. 2).

The experiment is connected with several difficulties. After the solidification of the pitch poured in molten state into the gutters (put horizontally) the central parts become lower than the parts near the border of the channel and some pitch must be added. In order to make the free surface to be plane and to come close to the borders, I have used a sufficiently hot flat-iron but nevertheless the deflections from the ideal plane could often attain 0·5-1 mm., what could cause a variation of 1-5% in the values of velocities at different points of the gutters. Besides it was difficult to assure the regular alimentation in the upper parts of the gutters and the regular outflow of pitch at their lower parts. Therefore I rejected usually the displacements of several upper and lower lines and introduced corrections, although not quite certain for the vertical deflections of different points of the surface of pitch from the upper surface of the gutter. In the experiments of 1909 (*13*, *14*, *15*) the discordances between the results were very small as can be seen from Table II giving an example of measurements taken on an amplified image of the photograph of one of the gutters. The data of Table II are the mean displacements (for several lines)—in mm. of the successive transversal lines at different distances *d* from the border the individual displacements differing from the mean values by 1-6 mm. The experiments of 1910 give greater discordances on account of the above-mentioned breakings of the lines made in glue-point.

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[1] Ann.d. Phys., 32, 777—808, 1910.

TABLE II.

d =	0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50
Lines 2-5	12	41	81	128	173	214	246	266	277	279
,, 6-10	16	50	92	135	177	213	241	261	272	274
,, 11-15	15	45	83	130	169	205	237	262	275	279
,, 16-17	8	40	72	132	181	222	251	262	277	277

TABLE III.

d =		0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
1909 ⊔ <	obs.	0·290	0·543	0·762	0·937	1·083	1·198	1·282	1·343	1·373	1·383
	theor.	0·295	0·547	0·759	0·936	1·080	1·194	1·280	1·340	1·376	1·387
V <	obs.	0·037	0·112	0·206	0·310	0·409	0·496	0·573	0·627	0·663	0·673
	theor.	0·045	0·121	0·213	0·313	0·410	0·496	0·567	0·621	0·654	0·665
◡ <	obs.	0·263	0·483	0·710	0·912	1·080	1·217	1·299	1·389	1·426	1·441
	theor.	0·273	0·514	0·729	0·914	1·071	1·200	1·300	1·371	1·414	1·429
1910 ◡ <	obs.	0.271	0·498	0·707	0·888	1·073	1·207	1·306	1·390	1·434	1·449

In the experiments of 1909 we can notice a slight excess of velocities in the middle parts in comparison with the theoretical distribution and a small deficiency near the borders—see Table III. This circumstance may be explained by the assumption of a greater value of η of the upper layers which have been treated with the flat-iron. These discordances were still more marked in the experiments of 1910 where the pitch was poured in the gutters in two portions and in the second portion was probably somewhat superheated. The probability of such an explanation becomes greater if we compare the values of η which I computed from the displacements of the upper layer —η_{I} in the Table IV—with the values—η_{II}—computed from the quantities of pitch which have flown out of the gutter.

TABLE IV.

	⌣	◡	V	⊔
$\eta_{I} \cdot 10^{-6}$	7·5	8·0	5·7	6·4
$\eta_{II} \cdot 10^{-6}$	6·0	5·7	6·2	5·6

The method of channel represents a special interest for the verification of the capillary theory of glaciers (*54*). This can be done (*23*) by means of preparing a gutter having the section of the studied glacier [1] and by comparing the displacements of the free surface of pitch filling this gutter when inclined, with the actual displacements of the ice at the surface of this glacier.

The formulae relating to the flow in channels of different sections are but slight variations of formulae relating to tubes and given by *Graetz*[1] and are reproduced in my article of 1912 (*23*).

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[1] In order to facilitate the finding of the sections of glaciers I have proposed an electrical drill by means of which the ice is fused by *Joule's* heat without being broken mechanically—*Vide* Zeits. f. Gletscherkunde, 8, 214-217, 1912.

III. *Flow between two immovable walls.*—If these walls be planes that would give (*49*) two additional methods of studying the slow transformations of solids or the laminar motion of a viscous liquid: the flow between two parallel planes under the action of gravity and the pressing through such an interstice. The first case was partly realized in the deflections of the lower surface of the parallelepipeds of *Dudeckij*—*54*, fig. 14—from planes; the second has not yet been the subject of experimental studies.

The case when the two immovable walls are coaxial cylindrical surfaces was studied theoretically by me (*48*) and this study as well as our experiments on asphalt (*21*, *24*, *25*, *26*, *29*) gave to *G. V. Grdina* (*45*) the possibility to answer the practical question whether and at what conditions can asphalt be used for the joints of the waterpipes. Experimentally this case of motion was studied by *T. Lonsdale*[2] with special purpose of investigating the critical conditions of passing from the laminar motion to the turbulent.

7. *Flow between immovable and movable walls.*—To this category belong the methods 2, 3, 4, 5, 6 and 10 of those which are enumerated in the pages 231-234 of the article *53* and which have been the subject of experimental studies. I may add only that the case of one immovable and one movable planes seems to take place under any slipping slides—namely, under the back portion of it, the front portion being the seat where the work of the forces of friction is sufficient only to raise the temperature up to the melting point of ice and the sequent portion having under it partly ice and partly water. Only under the back portion of a slide the work of the forces of friction is spent on transforming ice

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[1] Zeits. f. Math. u. Phys. 25, 316, 375, 1880.

[2] Phil. Mag., *46*, 163-169, 1923.

into a thin layer of water and the latter is pressed out sideways—seemingly moving laminarly (*51*, *52*).

The laminar motion between an immovable wall and a movable surface acting on the layer between, by forces which can be assumed equal to zero is realized still more quotidiously—in the laminar layer contiguous to any wall in the case of a turbulent flow (see § 2 above).

8. Results of study of resistance of solids to laminar motion of a viscous liquid.

If we exclude the previous investigations on the *Stokes* case of a falling sphere—method 14 (*53*)—where the velocity could be varied only by means of changing the density or the dimensions of the sphere, the researches of this kind were commenced by the investigation of *Gostjunin* and *Le Dentu* (*22*) to whom I have proposed to study the resistance of pitch to the motion of a cylinder. The pitch was contained in a long tube 20 cm. wide and the cylinder had a diameter equal to 18·7 mm. and an adjustable length up to 510 mm. and was provided with conical prow and poop. The general disposition of the experiment may be seen from figs. 3 and 4 in Plate XIII.

In spite of considerable acting forces f (equal to the nett difference of weights minus the friction of pulleys) varying from 4 to 10 kg. the velocities did not surpass 0·25 mm./min. and the way of the "vessel" along the tube in one direction lasted often several days. Such a duration of the experiment connected with the uncertainty regarding the true value of the mean temperature inside the pitch, diminished the agreement of the results which can be seen from the following Table V. Table V gives for different values of f and of l the mean values of the velocities of the vessel reduced to 20° and to the weight of 1 kg. on the assumption of the proportionality between the velocity and the acting force and expressed in 10^{-4} mm./min.

TABLE V.

$\frac{f}{l}$	4 kg.	6	8	10	Average observ.	Calculated.
0 mm.	225 ∓2	242 ∓3	230 ∓2	235 ∓2	231 ∓3	231 ∓15
56 „	210 ∓2	213 ∓3	215 ∓1	235 ∓8	214 ∓3	219 ∓14
113 „	228 ∓8	253 ∓10	246 ∓11	249 ∓8	243 ∓6	209 ∓29
169 „	213 ∓9	187 ∓7	220 ∓14	208 +7	202 ∓7	200 ∓28
540 „	—	—	—	154 ∓2	154 ∓2	155 ∓5

The calculated values were computed by means of the formula

$$f_1 = x + yl \qquad (5)$$

where f_1 is the force necessary to produce a velocity equal to 1, x is the "prow" resistance and y the lateral resistance for unit length of the cylinder.

In order to possibly diminish the influence of temperature and the duration of experiment in numerous further experiments (*32*) and (*38*), was used a less viscous liquid more than 800 kg. of a 85% solution of WW colophonium in turpentine-oil having an η of the order 10^5 which was contained in a bassin 3-4 meters long, 0·76 wide and 0·4 high. The "vessel" was towed by means of metallic wires passing through little holes in the end sides of the basin and over four pulleys as in the experiments of *Kuznecov* the scheme of which is illustrated by fig. 6 (see below). The vessels had respectively the diameter equal to 37·4, 18·7 and 9·4 mm. and a variable length equal to several times the maximal value 1080,554 and 301 mm.

Unfortunately the liquid used had a tendency to crystallize—a circumstance which caused considerable difficulties in these experiments, in which were pulled through the liquid simultaneously three vessels. One of these was in each series unchangeable and played a controlling rôle for giving means to reduce the observations to a common temperature.

Special measurements were made for determining the force necessary for towing the wire without any vessel; unfortunately no special experiments were made in order to separate the part of this force which was due to the resistance near the hole and which is possibly a considerable part of the whole. Table VI gives the results of computations—by means of the formula (5) — based on the assumption of the "hole-resistance" being equal 1°—to 0 and 2°—to half of the total resistance experienced by the wire.

TABLE VI.

	x_1	x_2	y_1	y_2
Vessel No. I	816	800	0·85	0·65
" " II	587	533	0·56	0·43
" " III	354	310	0·50	0·30
Wire	...	..	0·40	0·20

The data of this Table show that with the vessels used only when their lengths were becoming 30—100 times greater than their diameters, the prow-resistance would be equal to the lateral resistance. Although based on 90 series of runs to and back of the three vessels (with 3 different acting forces and 5 different lengths for each) the data of Table VI have a moderate precision on account of disturbing circumstances one of which was the unexpectedly great value of the resistance to the motion of the wire.

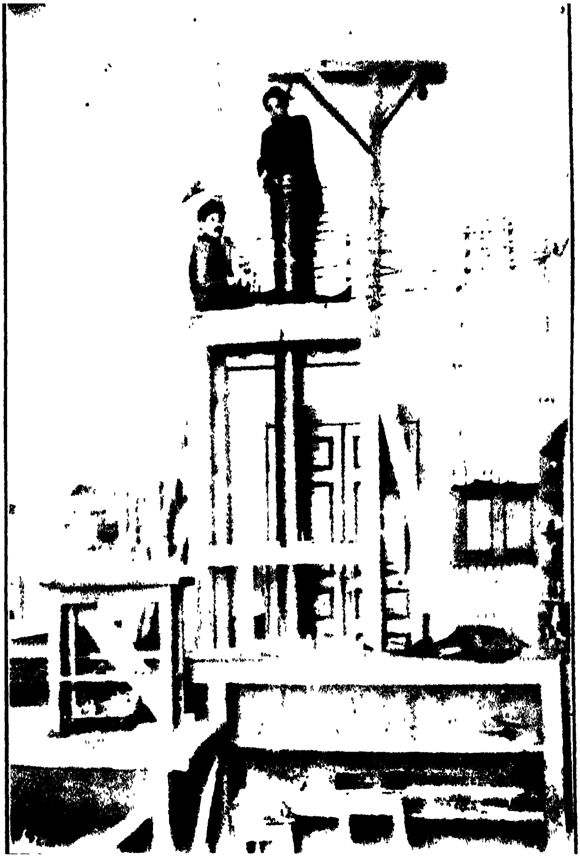

Fig 3

Photograph of the big vertical tube with pitch

Therefore better results were obtained by means of closed tubes filled with a viscous liquid and containing the solid—a cylinder with conical extremities (*38*) or a sphere (*32*, *37*). Fig. 5 represents, for example, the apparatus used by *Alfimov* and myself for studying the resistance of a sphere falling through a viscous liquid in a tube. In these experiments the tube (d=92 mm.) was made of metal with three mica-windows and could be narrowed by inserting into it similar tubes of 65 and 50mm. diameter.

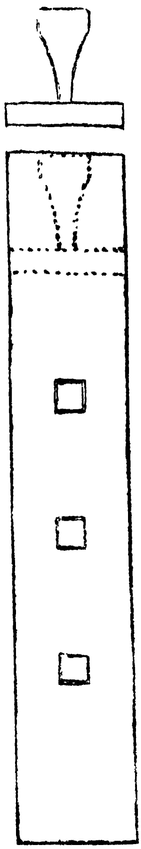

Fig. 5.

The motion of the steel ball (d= 19·2mm.) in a 75% solution of dammar in turpentine-oil was followed by means of a cathetometer by noticing the moments of passing over its central line of the lower and upper rand of the ball after it was laid at the top of the column of dammar and the lid pushed down and after the tube was reversed. Table VII shows an example of the results of observation.

TABLE VII.

Window.		Reading of the cathetometer.	Moment of passing of lower and of upper rand of the ball.				Tempera-ture.	Mean velocities in mm./sec.	
			min.	sec.	min.	sec.			
I	...	673·50	0	00	13	35	16·4	0·0235	
									0·0235
II	...	595·45	54	10	68	18	...	0·0236	
									0·0235
III	...	519·75	109	06	122	41	...	0·0235	
III	...	571·90	0	00	13	40	..	0·0233	
									0·0233
II	...	494·00	56	03	69	43	...	0·0233	
									0·0233
I	...	417·20	111	18	125	00	16·0	0·0232	

In these experiments the influence of temperature was again very sensible: even the illumination with an electric lamp—just for the time of the passage of ball near the window—caused considerable perturbations. The illumination by day-light necessitating the approach of the tube to the window of the underground room where the experiments were conducted, caused smaller but still perceptible perturbations.

In the experiments with cylinders were therefore used four adjacent glass tubes (150 cm. long) one of which was a controlling tube and contained invariably a steel ball and in the other three tubes 10·4, 28·2 and 17·1mm. wide were placed three cylindrical vessels of different widths ($d=12{\cdot}5$, 8·0 and 5·7mm.) and of variable length and weight; the tube in which each vessel was inserted was also interchanged from one series to the other.

The results can be seen in Table VIII where the three horizontal partitions correspond to full lengths of the cylinders No. 1, No. 2 and No. 3, to half lengths and to zero lengths (prow and poop conical extremities connected together directly). The application of formula 5 to these experiments gives unsatisfactory results, as can be seen from the values of x and y in Table VIII; T's are here the times in sec. for passing an equal length of 14 cm. reduced to equal time of the falling of the ball in the controlling tube and to equal acting force of 50 gr. for cylinder No. 1, 25 gr. for No. 2 and 10 gr. for No. 3.

TABLE VIII.

Cylinder Tube.	No. 1.			No. 2.			No. 3.		
	T	x	y	T	x	y	T	x	y
I	4450	−161	127	1129	+49	45	446	−23	38
II	7295			2074			522		
III	46840			3645			960		
I	2140	−74	203	589	+34	85	206	+22	41
II	3600			1054			268		
III	22910			1857			473		
I	80	−895	1315	135	+59	149	53	+2	78
II	310			204			104		
III	1600			367			153		

The values of x are partly *negative*, which can be explained by the influence of prow and poop extending at a considerable distance from them when the quotients of the diameters of the "vessels" in comparison with the transverse dimensions of the recipients (0·13-0·73 in these experiments whilst in the experiments in the large basin it was 0·06-0·25).

The values of y are more reliable as can be seen from Table IX giving the quotients of y to the values deduced theoretically (*38* and *48*) ; the average of these values being $1{\cdot}97 \mp 0{\cdot}15$ (instead of 1, as can be explained by the uncertainty of the value of η) and the maximum of these 9 values being 1·9 times as great as the minimum, whilst the quotient of corresponding values of y in Table VIII is 35.

TABLE IX.

D d	12·5	8·0	5·2
40·4	2·66	1·71	2·15
28·2	2·16	2·06	1·67
17·1	2·20	1·40	1·77

As another proof of the concordance of the data on lateral resistance of cylinders with the theoretical formula which considers the motion as the pressing of the liquid through the annular space between the cylinder and the walls by the acting force, I may mention that the quotient of lateral resistance of vessels I and III, the mean values of which are given in Table II (for the vessel II the data are less certain because it has been the controlling one in this series) was varying from 0·46 to 0·59, the theoretical value of the quotient being 0·51.

A similar standpoint is useless in the case of a sphere moving in a cylindrical tube of a radius R not too great in comparison with the radius r of the sphere because the theory of Ladenburg,[1] leading to the formula

$$f_{\mathrm{R}} = f_{\mathrm{R}=\infty}\left(1+2\cdot4\frac{r}{\mathrm{R}}\right) \tag{6}$$

can be deduced only for small values of r/R. For greater values of this quotient corresponds somewhat better the experimental formula

$$f_{\mathrm{R}} = f_{\mathrm{R}=\infty}\left(1+3\cdot3\frac{r}{\mathrm{R}-r}\right) \tag{7}$$

which for instance gives for the experiment of *Alfimov* and myself mentioned above the values: 0·0486, 0·0406 and 0·0471 for the three tubes used. The experiments of *Bolotov* and *Goroh* (*37*) give similar results.

A detailed research of the same kind was made by *Kuznecov* (*28*) who was studying the resistance for the motion of a quadratic plate (a=3·5, 5·0, 7·0, 10·0 and 17·0 cm.) moved in a gutter of rectangular section (width A= 15, 22 and 30 cm.). The gutter was filled with a solution of pitch in petroleum having an η equal to $9\cdot10^4-4\cdot10^4$ according to the temperature. The disposition of experiments can be seen from figs. 5 and 6. *Kuznecov* has made observa-

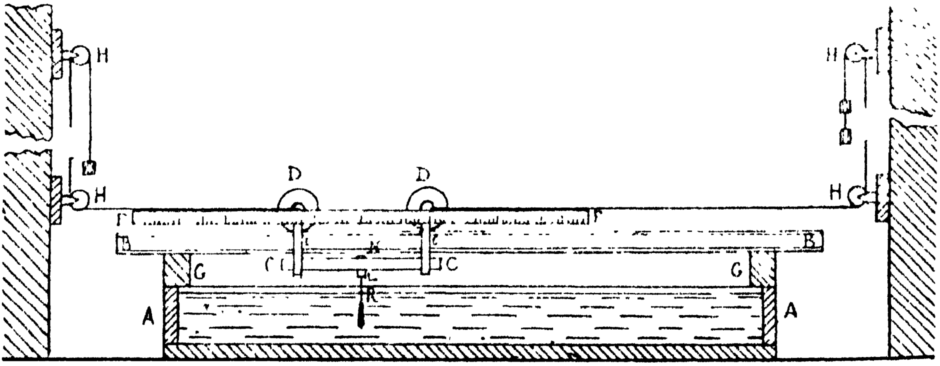

FIG. 6.

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[1] Ann. d. Phys., *28*, 447, 1907.

tions at different angles of the plate relatively to the direction of motion, with spheres, etc., but special attention he paid to the motion of a quadratic plate set perpendicularly to this direction.

After careful study of forces of friction in the pulleys, in the axes of the carriage, of the wheels on the rail the author decided to measure (by means of a stopwatch or a chronograph) the interval of time which was necessary to pass a quite definite piece of the rail being moved by the difference of the weight on either side, their *sum* being kept constant. Excessively great differences were not used on account of a too big wave moving in front of the plate and disfiguring the phenomenon. The influence of the resistance of the slab K (fig. 7) holding the plate was eliminated by means of observing the velocity at different depths of the plate.

The results were expressed by the author by an experimental formula

$$f_1 = \alpha\eta a^3\left[1+\frac{\beta}{(A-a)^3}\right] \qquad (8)$$

where f_1 is the force necessary to produce a velocity equal to 1. In order to find the most probable values of the co-efficients α and β, *Kuzncov* used one long series of observations with different plates in the channel of 30 cm. during which the temperature of the room has been very steady and coincided with the temperature of the pitch solution. With these values of α and β and the values of η corresponding to the temperature $\theta°$ of the experiment, he has calculated the values of f_1 and compared them with the observed values. Even for small values of a by which the correction on the resistance of the slab sometimes exceeded the values

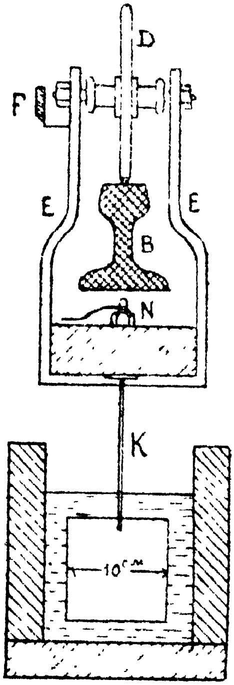

Fig. 7.

of f_1 the agreement between the observed and the computed values is quite satisfactory, as can be seen from Table X which gives the results for several *series* of observations where f_1 varied in a proportion of 1 to 230. Same is true for *isolated* observations not included in this Table X.

TABLE X.

λ	$a =$	13		10	7		5		3·5
30	θ	17·6		17·6	17·6		17·6		18·2
	f_1 obs ...	2510		1380	654		372		116
	f_1 calc .	2560		1390	615		321		126
22	θ	16·5		16·4	16·1		16·5		16·5
	f_1 obs ..	5980		2640	1130		500		260
	f_1 calc .	5970		2690	1100		508		238
15	θ	20·2	17·0[1]	21·0	16·8	20·7[2]	16·8	20·7[2]	16·8
	f_1 obs .	27300	32000	2210	1615	576	741	215	339
	f_1 calc ...	27100	62000	2120	1815	647	724	254	308

This agreement shows clearly the applicability of the method. It would be desirable also to make use of the method of constant velocity instead of constant force and to move the solid by means of a clockwork measuring the force of traction by means of a stretched spring.

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[1] "A cascade of pitch."

[2] The temperature of the room; the temperature of pitch not noted

18

X-Ray Diffraction in Liquids*

BY

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(Plates XIV, XV, XVI and XVII.)

(Received for publication on 8th April, 1927.)

Abstract.

Previous experimental work in this field is summarised and it is shown that the available data are rather meagre and not sufficiently precise.

A *review* is made *of the theories so far proposed*, and in particular, of the theory of Raman and Ramanathan which extends the thermodynamic theory of light-scattering in liquids to the X-ray region.

Improvements made by the writer in the technique are described. (*a*) the usual glass or celluloid containers which give liquid-like patterns themselves, have been replaced by a cell with mica windows, (*b*) the incident pencil used has been made narrower. By thus avoiding the complications due to the container and also getting a better resolution of the phenomenon, the variations in the diffuseness of the halo and differences in its structure for different liquids are clearly revealed. 22 liquids belonging to the aliphatic and aromatic groups have been studied.

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* Contribution from the Laboratory of the Indian Association for the Cultivation of Science, Calcutta.

It is shown that *the agreement* obtained in a few cases by Keesom and Smedt *between Ehrenfest's formula* and *the mean molecular distance* as calculated on the assumption of hexagonal closest packing *is purely accidental*. That the assumption of close-packing is not justified is shown very clearly by the data for the long-chain aliphatic compounds. The ratio k which the distance between the diffracting planes given by Bragg's law for the principal halo bears to the quantity $n^{-\frac{1}{3}}$, where n is the number of molecules per unit volume, has been calculated for several liquids, and it is found that the value of *k departs more and more from that corresponding to close-packing as the length or asymmetry of the molecule increases.* k ranges from 1·05 for water to ·603 for the long molecules of oleic acid. The value of k for cyclo-hexane (·924) is quite different from that for hexane (·808) but is nearly the same as that for benzene (·926) which possesses a molecular structure similar to cyclo-hexane.

The influence of compressibility on the sharpness of the halo predicted by the theory of Raman and Ramnathan is confirmed. *The scattering at small angles* is not negligibly small, and is relatively greater in the case of liquids with *higher compressibility* or having *comparatively unsymmetrical* molecules than for the others.

A study of over a dozen benzene derivatives shows an interesting variety in the structure of the principal halo. In ortho- and meta-nitrotoluenes, and in mesitylene, the halo appears clearly resolved into two components. The progressive way in which the halo is modified as we pass to more and more complex derivatives and the distinct differences found even between the patterns of isomeric molecules, reveals *the importance in X-ray liquid-diffraction of the form and structure of the molecules.*

CONTENTS.

1. Previous Experimental work.
2. Review of Theories.
3. Improvements in technique and results.
4. Radius of principal halo.
5. Relation of Diffuseness of Halo to Compressibility.
6. Scattering at small angles.
7. Influence of Molecular Form and Structure.

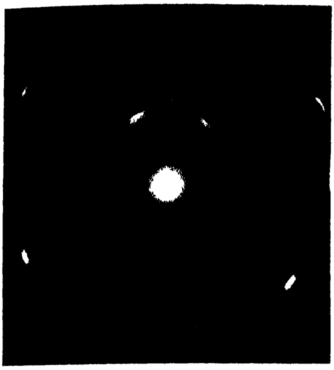

Fig. 1. Pentane

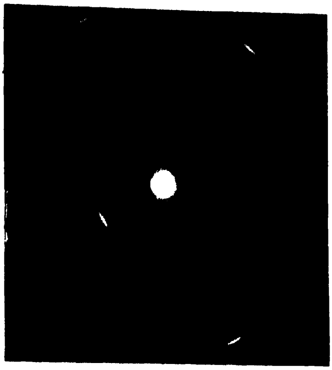

Fig. 2. Ether

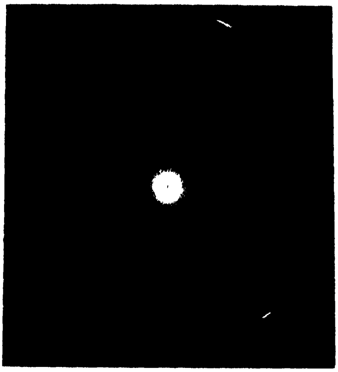

Fig. 3. Water

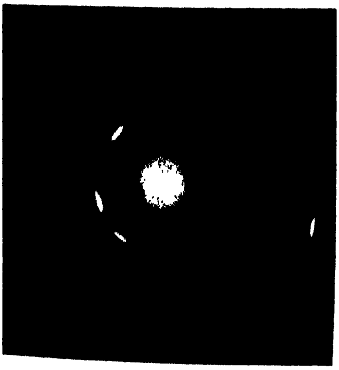

Fig. 4. Hexane

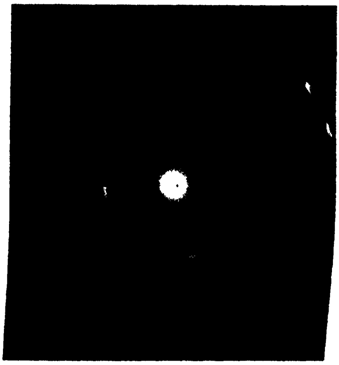

Fig. 5. Heptane

1. *Previous Experimental work.*

The history of X-ray diffraction in liquids begins with an observation by Debye and Scherrer[1] made in the course of their work on X-ray diffraction by irregularly oriented substances. They found that when a narrow pencil of monochromatic X-rays was made to pass through a thin layer of liquid and received on a photographic plate, the X-rays scattered by the liquid gave rise to a more or less sharp circular halo, separated from the direct spot by a relatively clear space. It is interesting to note that in the case of benzene, these authors directly employed a thin stream of the liquid. This is the only case in which the container was dispensed with altogether. In all the other measurements made so far, use has been made of cells or tubes of glass, collodion or some other material known to give a diffraction pattern exactly similar to that of a liquid. It may also be mentioned that the powder-photograph method of Debye and Scherrer has been used by all the later investigators with the exception of Hewlett[2] and G. W. Stewart[3] and his co-workers, who used the ionisation method.

Long after, Debierne[4] examined some liquids, *e.g.*, mercury, methyl iodide, methylene iodide, benzene, brombenzene, etc., and some mixtures, and got results similar to those of Debye and Scherrer.

Later, Hewlett[2] who used the ionisation method studied the three organic liquids, benzene, octane and mesitylene, and obtained scattering-curves for them, in which the intensity of scattering has been plotted as a function of the angle of scattering. The liquids were contained in thin celluloid capsules and were irradiated with the $K\alpha$ line of molybdenum from a molybdenum target Coolidge tube. We shall quote the results obtained for benzene which are typical. The ionisation curve for benzene shows a maximum at 8·5°, the intensity falling more quickly at smaller angles than at larger. The fall of intensity is, however, fairly slow even on the small-angle side of the maximum, the curve showing an intensity of 50% of the maximum at 4° and 35% at as small an angle as 2·5°. These rather large values of scattering at such small angles are altogether contradicted by a mere glance at the hitherto-published photographs of the liquid-halo, and more particularly by the photometric results for benzene published by Wyckoff[1] in his paper on liquid mixtures. It may be mentioned here that there are no other measurements of intensity distribution available besides these two. Even Wyckoff's values at small angles must be too high on account of the rather broad incident pencil in his experiments.

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[1] P. Debye and P. Scherrer, Nachrichten Göttingen, Vol. 16, 1916, p. 16.

[2] C. W. Hewlett, Phys. Review, XX, 1922, p. 688.

[3] G. W. Stewart and others, Phys. Rev., Vol. XXVII, Series 2, 1926, p. 104.

[4] A. Debierne, Compt. Rend., 173, 1921, p. 140.

A few liquids including liquid O_2, N_2, A, H_2O and half a dozen organic substances have been examined by Keesom and Smedt.[2] [3] In their first paper,[2] the Kα line of copper was employed, and in the second[3] the Kα line of molybdenum. Some of the liquids were common in the two papers and their haloes obtained with different wave-lengths did not show any difference except in the angular radius which is reduced proportionately to the value of λ. In some cases, *viz.*, those of water, O_2, N_2 and A, a feeble second ring also has been observed outside the principal halo by these authors. This second ring is, however, not at all separated from the principal halo and appears as though it were a continuation of the latter. Measurements of the angular radius of the principal halo for the various liquids are also given in these papers.

Diffractions in half a dozen polymerised liquids, such as paraldehyde, benzaldehyde, benzyl benzoate, etc. have been studied by Smedt[1] who has again found in the two cases of butyric acid and benzaldehyde the second halo observed by Keesom and Smedt and mentioned in the previous paragraph. In one case of benzyl benzoate, measurement has been given of a third halo also. Unfortunately, however, none of the photographs has been published and it is very difficult to form an idea of what the third halo may have been like. Anyhow, it is quite clear that the third halo must have been excessively feeble, much feebler than the second one. Lastly, mention might be made of some experiments recently made by Prins[2] (referred to by Zernicke and Prins[3]) which it is stated, confirm the observation that the intensity of scattering at small angles is very small.

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[1] R. W. G. Wyckoff, Am. J. of Science, V, 1923, p. 460.

[2] Keesom and Smedt, Proc. Roy. Soc., Amsterdam, XXV, 1923, p. 118.

[3] Keesom and Smedt, same proceedings, XXVI, 1923, p. 112.

A mention of the behaviour of liquid crystals, amorphous solids, and glasses may perhaps not be out of place here. The experiments of Hückel[4] with liquid crystals, of Friedrich[5] with amorphous solids and of Jauncey[6] with glass show that these three classes of substances give diffraction patterns similar to those of the usual isotropic liquid.

Diffraction measurements have also been obtained by Wyckoff[7] for some pure liquids and their 1 : 1 mixture by volume, as also of some concentrated aqueous solutions. The photometered results obtained show that so far as these preliminary experiments go, the diffraction pattern of a mixture of two liquids can be regarded as a simple superposition of the patterns of the component liquids. The patterns of concentrated aqueous solutions of potassium chloride and iron ammonium alum have, however, been found to be identical with those of water.

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[1] De Smedt, Bull. de la classe des Sciences, academie royale de Belgique, 10, 1924, p. 366.

[2] J. A. Prins, Physica, 6, 1926, p. 315.

[3] F. Zernicke and J. A. Prins, Zeits. fur Physik. 41, 1927, p. 184.

[4] Hückel, Phys. Zeit, 1921, p. 561.

[5] Friedrich, Phys. Zeit, 14, 1913, p. 317.

[6] Jauncey, Phys. Review, XX, 1922, p. 405.

[7] Loc. Cit.

From the above survey it would be clear that the subject of X-ray liquid diffraction is still in its infancy. The results available are rather meagre and not sufficiently precise. The present investigation was undertaken at the suggestion of Prof. C. V. Raman in order to study the phenomenon more thoroughly both from the experimental and theoretical stand-points.

2. *Review of Theories.*

The essential features of X-ray liquid diffraction as disclosed by the work reviewed above, are (1) that the intensity of scattering at small angles is small, (2) that a considerable part of the scattered energy appears within a certain rather small range of angles, thus forming a marked halo detached from the direction of the primary beam and (3) that in some cases, at any rate, an appreciable proportion of the scattered energy also appears at still larger angles of diffraction. The fact that the size of the halo changes proportionately with the wave-length shows conclusively that the phenomenon is to be ascribed to diffraction. The moderate sharpness of the halo reminds one of the powder pattern and points to a certain regularity of arrangement of the diffracting centres, namely, the electrons.* Now in building up a mass of liquid from its ultimate particles, namely, the atomic nuclei and electrons, we have three well-defined stages in the building-up process, namely, the atom, the molecule and finally the assemblage of molecules going to form a finite mass of the liquid. The arrangement of electrons throughout the liquid has therefore to be divided into three similar stages.

1. The arrangement of electrons in the atom.
2. The arrangement of atoms in the molecule.
3. The arrangement of molecules in the liquid.

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* The masses of atomic nuclei are so large that their contribution to the scattered energy is neglible compared with that due to the electron.

A complete theoretical investigation will obviously have to take into consideration all these three factors together.

(1) *The arrangement of electrons in the atom.*—This factor has not at all been considered so far in connection with liquid-diffraction. It is, however, the same as the F-factor with which we are already familiar in crystal-diffraction. Taking into consideration the peculiar distribution of electrons in a particular atom, the relative phases of the waves scattered by them separately can be determined, and the resultant amplitude calculated according to the well-known laws of interference. The problem is no doubt complicated by the fact that the electrons being in motion have no fixed positions but making certain justifiable assumptions about averaging of the orbital positions, the problem has been successfully solved by a number of investigators. Hartree[1] has calculated the values of F for various ions as functions of the glancing angle for Mo Kα X-rays. The values for any other wave-length is easily found because the expression for F involves

$$\frac{\sin\beta}{\lambda},$$

β being the glancing angle. It will be seen from Table V in Hartree's paper that the value of F for O^{-2} at $\sin\beta = \cdot 15$ is 64% of that for $\sin\beta = 0$. This is the range of angles with which we are concerned in liquid diffraction. In the case of lighter ions F diminishes still less with β. It is therefore obvious that in the case of organic liquids composed of light atoms like C, N, O this factor is not very important and these atoms can be regarded as scattering nearly uniformly in all directions with which we are practically concerned. The same thing is also true for the heavier ions right up to Tl^{+3} as a glance at the same table in Hartree's paper will at once show.

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[1] D. R. Hartree, Phil. Mag. L., 1925, p. 301.

(2) *The arrangement of atoms in the molecule.*—Not much has been done in this connection either. Only two attempts have been made, the one by Debye and Scherrer[1] who have considered the case of a benzene molecule and the other by Ehrenfest[2] who has made calculations for a diatomic molecule. Assuming that the benzene halo is due solely to the interaction of the atoms in the molecule and ignoring factors (1) and (3) for this case, a calculation was made of the scattered intensity in different directions.

The case of a diatomic molecule considered by Ehrenfest is a little simpler than the case of a benzene molecule. By considering the molecule axis to possess all possible directions and averaging, an expression has been derived for the intensity as function of scattering-angle which is a continuous curve with the highest maximum in the direction of incidence, the intensity changing oscillatorily as the scattering-angle is increased.

From the agreement of the size of the benzene-halo with one of the secondary maxima in his curve, Debye had suggested that the liquid-haloes owe their origin to the structure of the molecule. This suggestion is negatived by the fact that monatomic liquids like argon and mercury possess a halo similar to that of substances with more complex molecules.

(3) *The arrangement of molecules within the liquid.*—The analogy between the liquid-haloes and the crystal powder patterns has led certain writers to suggest that a liquid may be considered as consisting of crystal fragments. This rather crude supposition can, however, hardly be regarded as worthy of detailed discussion in our present state of knowledge.

An attempt to develop a theory of X-ray diffraction based on established ideas about the nature of the liquid state, was made by Raman and Ramanathan.[3] Keesom and

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[1] Loc. Cit.

[2] P. Ehrenfest: Pro. Roy. Acad. of Sciences, Amsterdam, XVII, part 2, p. 1184.

[3] C. V. Raman and K. R. Ramanathan, Proc. of the Ind. Ass. for the Cult. of Science, Vol. VIII, Part II, 1923, p. 127.

Smedt who make use of Ehrenfest's calculations for a diatomic molecule, consider only the interaction of two neighbouring molecules and although their work emphasises the importance of this factor of the spatial arrangement of the molecules in liquid diffraction, it does not go far enough. For a proper consideration of this factor, we have to consider not two neighbouring molecules alone, but the whole assemblage of them together. Keesom and Smedt[1] calculate the distance between the interfering particles using the known wave-length and the observed angular size of the halo, and identifying the latter with the first outer ring surrounding the principal maximum in the direction of the primary beam, given by Ehrenfest's formula. They find in the cases studied by them a fair agreement between the inter-molecular distance thus determined and the value calculated from the density of the liquid on the assumption that the molecules are in the hexagonal closest-packed arrangement. The assumption that the molecules of a liquid are close-packed is, however, *prima facie* very hard to justify. If it were true, the diffraction-haloes should approach those of a crystal-powder in sharpness, which is far from being the case. We shall have occasion to refer to this assumption and discuss it more fully in sec. 4.

The theory of Raman and Ramanathan is based on the fundamental idea that the molecules in a liquid are not arranged at random, but that the arrangement possesses a certain degree of regularity which may go far towards explaining the diffraction-halo found in the liquid pattern.

Although the molecules in a liquid are not arranged with the perfect regularity with which the units in a crystal are arrayed, it is none the less true that their arrangement is not so chaotic as in the case of a gas. Judging from the specific volume in the three states of matter, it will not be wrong to say that in respect of the arrangement of the molecules in space, the liquid state is more closely related to the solid than to the gaseous state. This regularity of arrangement which one would expect from these simple considerations can be estimated thermo-dynamically from the compressibility of the fluid.

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[1] Loc. Cit.

In their treatment, these authors have extended to the X-ray region the idea of density-fluctuations deduced from the statistical-thermo-dynamical theory developed by Smoluchowski[1] and Einstein[2] for the case of light-scattering and amply verified in that region. Why and how far the idea has been modified to suit the X-ray case will be clear shortly.

The only difference between light-scattering and X-ray scattering is the one in the order of the values of the wave-length, which in the case of X-rays becomes much less than the average distance apart of the molecules. Now the essential idea of the Einstein-Smoluchowski method is to treat a fluid as a continuous substance subject to local changes of density determined by thermo-dynamical considerations. This assumption is justifiable in the optical case, where the wave-length is much larger than the scale of molecular dimensions. The application of the theory depends essentially on the possibility of dividing up the medium according to the method of Lorentz into slabs of thickness $\lambda/2 \sin \frac{1}{2}\theta$, † which can be further sub-divided into slices, each of which is many molecules thick, so that the fluctuations of density in any slice can be assumed to be independent of those in the neighbouring ones. This is obviously possible when λ is large, namely, in the optical case. Even in the X-ray region, it would stand for very small values of θ, that is to say, for small angles of scattering. From actual data for compressibility, for benzene the authors have shown that according to the theory of Smoluchowski and Einstein, the energy scattered at 2° with $\text{MoK}\alpha$ for which the benzene-halo lies at 8·5°, would be very small.

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[1] M. V. Smoluchowski, Ann. der Physik, 25, 1908, p. 205.

[2] A. Einstein, Ann. der. Physik, 33, 1910, p. 1275.

† θ denotes the angle of scattering and is double the glancing-angle.

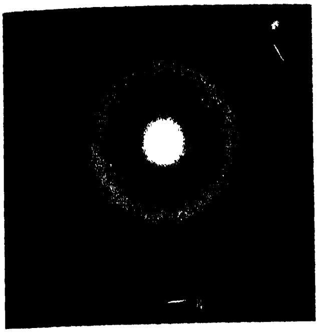


Fig. 6. Octane

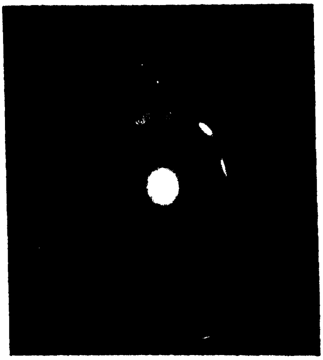


Fig. 7. Benzene

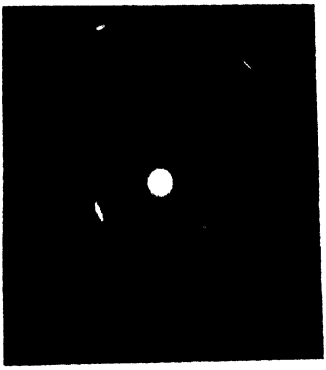


Fig. 8. Aniline

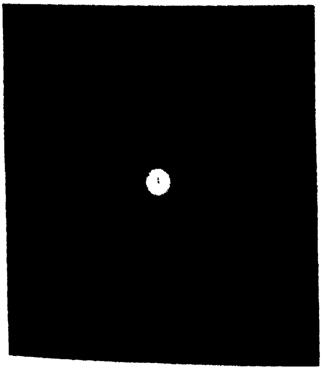
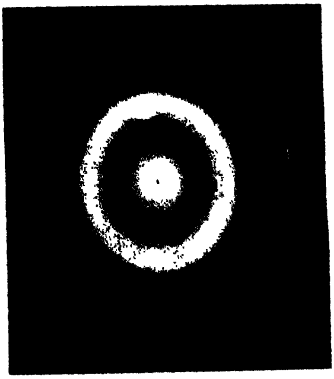


Fig. 9. Glycerine



For any moderate value of the angle of scattering θ, each slab of thickness $\lambda/2 \sin \frac{1}{2}\theta$, would be only a few molecules thick, and it would no longer be possible to assume that when it is sub-divided into thinner slices, the fluctuations in the different slices are uncorrelated or independent of each other. For instance, in the direction of the principal halo, each slab would, on the average, be just one molecule thick, and when it is further sub-divided into thinner slices, the fluctuations of density in these slices would be almost completely correlated in the direction of amplifying the total observed effect. The Smoluchowski-Einstein theory cannot therefore be applied, as it stands, to the problem of X-ray scattering except at very small angles of scattering.

For larger angles of scattering, therefore, the liquid can not be regarded as a structureless continuum, but its actual coarse-grained structure has to be taken into account. This has been done by applying Fourier analysis to the actual distribution of matter in the liquid, which is thus analysed in all directions into a structural spectrum, in other words, into a number of superposed periodic distributions of different wave-lengths. The law of the structural spectrum would obviously be determined by the size and structure of the molecules, their average distance apart and the fluctuations of the actual distance between neighbouring molecules from the mean value. Each periodicity of wave-length λ_1 giving, in a way, a periodic or regular crystalline arrangement, is responsible for scattering in a specific direction given by the well-known Bragg formula

$$\lambda = 2\lambda_1 \sin \tfrac{1}{2}\theta \qquad (1)$$

Ignoring, as a first approximation, all the factors which determine the law of the structural spectrum except the average distance-apart of the molecules and the fluctuations from it as controlled by the compressibility of the fluid, Raman and Ramanathan determine its general character and deduce the expression given below for the distribution of intensity in the diffraction-halo.

$$I=C_1 \text{ exp.} \left\{ -\frac{1}{16} \cdot \frac{N}{RT\beta} \lambda_0^3 \left(1-\frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\} \quad \ldots \quad (2)$$

where N and R are respectively the Avogadro-constant and gas-constant for a gram-molecule, T is the absolute temperature, β the isothermal compressibility, λ_0 the mean molecular distance, C_1 a constant, and λ_1 is the term involving the angle of scattering θ, and is given by expression (1) in which λ denotes the wave-length of the incident X-rays. From equation (2) it is easily seen that the maximum intensity corresponds to $\lambda_1=\lambda_0$, and therefore lies in the direction θ_0 given by

$$\lambda=2\lambda_0 \sin \tfrac{1}{2}\theta_0 \quad \ldots \quad \ldots \quad (3)$$

In other words the peak of the structural spectrum corresponds to a wave-length λ_0 equal to the mean molecular distance.

Equation (2) has been plotted by Raman and Ramanathan for benzene from a knowledge of the compressibility and found to be in fair agreement with the ionisation curve obtained by Hewlett[1] for the same liquid, except at small angles where the latter curve is in direct disagreement with the photometer curves of Wyckoff.[2] The value given by this theory for small angles is smaller than that shown by Hewlett's curve and this agrees better with Wyckoff's measurements. This agreement indicates that at least for benzene, the arrangement of molecules in the liquid is probably the most important factor, or at least more important than factor (2) corresponding to the internal structure of the molecule.

E. H. Collins[3] reports some tests of the Raman and Ramanathan theory in which he found that the diffraction-halo for ether-liquid which has a high compressibility is very

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Loc. cit. [2] Loc. cit.

E, H, Collins, Phys. Rev., XXVII, Series 2, 1926, p. 242.

diffuse as predicted by the theory. He found, however, that the agreement is only qualitative, which is not surprising in view of the approximate nature of the theory.

A further test of the theory would be to determine the influence of high temperatures on the sharpness of the halo, but this has not yet been done.

Recently a theoretical paper has appeared by Zernicke and Prins[1] which also considers this factor of inter-molecular arrangement. Their treatment, however, differs from that of Raman and Ramanathan whose paper seems to have escaped their notice, and is mostly one-dimensional. The interesting point about it is that the molecule is considered to be of finite size, and the law of free-path in the gas theory is applied to the free space between the molecules. The expression obtained gives for the liquid diffraction pattern a number of maxima at distances proportional to the square roots of the natural numbers. These flatten out as the compressibility (represented by the factor l in this treatment) increases. The treatment no doubt explains the small intensity of scattering at small angles but fails at larger angles, for even in the case of low compressibility ($l = \cdot 1$) the outer maxima should, according to this theory, have intensities comparable to the first one. As observed by the authors themselves in their introduction, these outer maxima have been observed only occasionally. They are exceptions rather than the rule and cannot be regarded as due to the general characteristics of the liquid state.

Lastly, a brief reference may be made to a paper by Brillouin,[2] in which an attempt is made to explain the phenomena of X-ray diffraction in liquids and amorphous solids on the basis of the quantum theory of specific heats. As, however, the predictions of the theory do not fit with the experimental facts which have come to light, we need not enter into a detailed discussion of it.

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[1] Loc. cit.

[2] L. Brillouin, Annales de Physique, January and February, 1922, p. 88.

From the above survey of the various attempts made in order to explain the phenomenon, it would be clear that emphasis has been laid only on one aspect of the problem or another. The subject has evidently intrinsic difficulties, inasmuch as the case of a liquid is not so simple as that of a crystal with its perfect regularity, nor even as that of an ideal gas with its absolute chaos. Our knowledge of the liquid state is far from satisfactory and a more complete understanding of the phenomenon naturally demands a more thorough experimental investigation.

3. *Improvements in technique and results.*

The arrangement of apparatus employed in the present investigation was the same as in the powder photograph method of Debye and Scherrer. As the source of X-rays a metal Shearer tube with copper anticathode was employed. The tube was excited with an induction coil working with a mercury gas interrupter. The exciting voltage was kept in the neighbourhood of 50 K.V. and the current in the X-ray tube about 9 m.a. As copper has a low atomic weight and as the voltage applied was moderate, the proportion of white radiation was relatively small and the X-rays used were fairly monochromatic, consisting mainly of Cu $K\alpha$ and $K\beta$. Further as the wavelengths of the $K\alpha$ and $K\beta$ lines are fairly close together and as the $K\alpha$ line is about 6 times as intense as the $K\beta$ line, the use of a filter to cut off the $K\beta$ line was not considered necessary for the purposes of this paper.

The experimental technique was improved in the following two directions (1) *Nature of the containing vessel.* The ideal arrangement would be to dispense with the container altogether. This is, however, not always convenient, and some sort of vessel or other has always been used. Occasionally, aluminium has been used. Celluloid and glass are, however, the two materials that have commonly been employed. Now these materials have a serious disadvantage, inasmuch as they too give a circular halo which will be superposed upon that of the liquid itself. There is great difficulty in disentangling the one from the other. This difficulty can perhaps be minimised considerably by the use of very thin glass tubes. But as it is by no means easy to blow excessively thin glass tubes of moderate bore, the best way of eliminating this disturbing cause is to use some crystalline material like mica at least as windows for the ingress and egress of the X-rays. A vessel with mica windows was constructed in a simple way as follows. A hole about 7 mm. diam. is made in the centre of a circular metal plate about 1·5 mm. thick. A thin sheet of mica ·005 mm. thick was pasted with soluble glass on either face of the plate in order to cover up the hole. The liquid was contained in the cavity between the mica sheets. For putting in the liquid and for allowing the displaced air to come out, two narrow channels were drilled inside the metal plate along two radii at about 30° apart. These channels were closed after putting in the liquid in order to prevent evaporation. The spots in the various figures of Pls. XIV-XVII are the Laue Spots due to the mica windows. These spots being only scattered here and there, the diffraction halo of the liquid stands quite disentangled from them and there is not the slightest ambiguity about its true nature. Further, directions can be found in each figure which are free from any spots, and thus the use of mica windows gives us nearly the same satisfactory results as the ideal arrangement of dispensing with the container altogether. (2) *Width of the incident beam.* Ideally, the beam of X-rays should be infinitely narrow. In that case alone the whole diffraction pattern will be completely resolved and the intensity at any point can be referred accurately to a definite angle of scattering. In practice, however, the width of the beam has to be finite. But the narrower the pencil the greater the chances of small differences in detail between different pictures being detected and therefore of small effects being discovered. The actual width of the beam used here can be calculated from the following data. The beam of X-rays was made to pass through a hole 3 cm. long and ·75 mm. diam. bored in a lead block 4·5 cm. long, the remaining length of 1·5 cm. being widened out to a diameter of 5 mm. in order to exclude the diffraction pattern of the lead diaphragm. The width of the pencil thus obtained is about half as small as that generally used previously. To illustrate the effect of making the beam narrow, it might be mentioned here that in preliminary pictures taken with a diaphragm 3 cm. long and 2 mm. diam., the halo for meta-nitro-toluene (Fig. 21) which now shows two clearly-resolved rings, could not at all be distinguished from that of nitro-benzene which shows a single wide halo (Fig. 15). Also the clear space now separating the nitro-benzene halo from the direct spot was altogether absent.

The present paper gives the results of a study of some two dozen liquids, all organic with the exception of water. They are taken both from the aliphatic and the aromatic groups and are all Kahlbaum's manufacture with the exception of glycerine, oleic acid and aniline, which were Merck's extra-pure. Glycerine used was bidistilled and the aniline and oleic acid redistilled just before use. Phenol was melted and kept supercooled at room temperature (25°C), while para-nitro-toluene was kept melted at 65°C. The last two substances were also Kahlbaum's. The distance between the photographic plate and the liquid cell was 3·25cm., and the exposure was 5 to 7 hours.

The following is a list of the various liquids studied.

1. Pentane,
2. Hexane,
3. Cyclo-hexane,
4. Heptane,
5. Octane,
6. Oleic acid,
7. Ether,
8. Glycerine,

9. Water,
10. Benzene,
11. Phenol,
12. Aniline,
13. Toluene,
14. Ethyl-benzene,
15. Nitro-benzene,
16. o-Xylene,
17. m-Xylene,
18. p-Xylene,
19. Mesitylene,
20. o-Nitro-toluene,
21. m-Nitro-toluene,
22. p-Nitro-toluene.

The results obtained are very striking. These are arranged in the following four sections. The various photographs will be found in plates XIV-XVII. By a mere glance at them, it will be clear that the halo is not by any means quite simple in structure in all cases. The benzene derivatives, particularly, show a remarkable and profound variety in the structure of their haloes. Even in the case of the aliphatic liquids where the haloes are of a simpler type, the sharpness of the halo varies in an interesting manner from liquid to liquid.

4. *Radius of principal halo.*

If we make the assumption that the liquid-pattern is due solely to the arrangement of the molecules in the liquid, and not at all to the inner molecular structure, the measurement of the angular radius of the halo must enable us to determine the mean distance between molecules which are now the diffracting centres for the scattered X-rays. Two different methods of interpreting the data have been employed, the one by Raman and Ramanathan[1] and the other by Keesom and Smedt.[2] We shall first consider the method of the latter who, as has been mentioned in sec. 2, have arbitrarily restricted themselves to the consideration of the inter-action between two neighbouring molecules only, and calculated the molecular

Loc. cit.

[2] Loc. cit.

distance *a* by the use of the following formula of Ehrenfest's for a diatomic molecule,

$$7{\cdot}72\,\lambda$$

where θ_0 is the angle which the direction of the principal halo makes with that of incidence. This can be rewritten in the form

$$a=\frac{\quad}{1{\cdot}63\sin\theta_0/2} \qquad \ldots \quad (4)$$

for the convenience of comparison with the expression of Raman and Ramanathan.

Keesom and Smedt have also calculated *a* theoretically on the special assumption that the molecules in a liquid possess the hexagonal closest-packed arrangement of spheres, and obtained some agreement between the theoretical and experimental values. On this assumption,

$$a=1{\cdot}33\sqrt[3]{\frac{M}{d}}\ \text{A.U.},$$

where M is the molecular weight and d, the density of the liquid. Remembering that the mass of an hydrogen atom is equal to $1{\cdot}663\times10^{-24}$ gm., and denoting the mass of the liquid molecule by m, we have

$$a=1{\cdot}123\sqrt[3]{\frac{m}{d}}$$

Let us now see whether this assumption of hexagonal close-packing is supported or not by the results of the present investigation. Table 1 contains the required data for a few of the liquids which possess the simple type of halo. It is clear that in these simple cases alone has the size of the halo

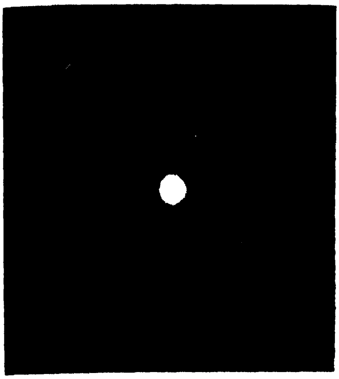

Fig. 11. Cyclo-hexane

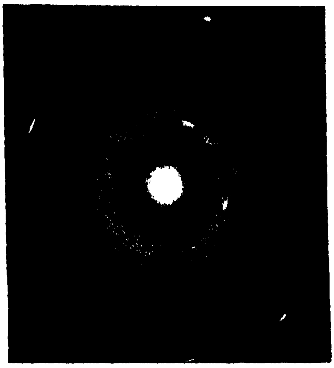

Fig. 14. Ethyl Benzene

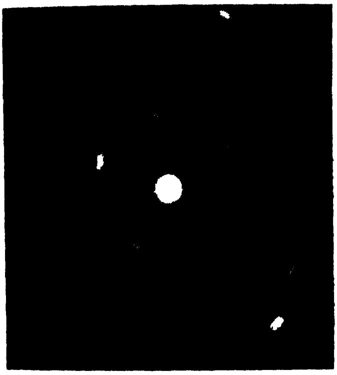

Fig. 12. Phenol

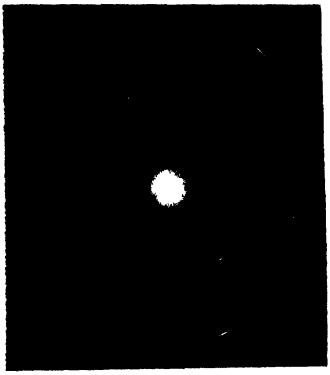

Fig. 15. Nitro-Benzene

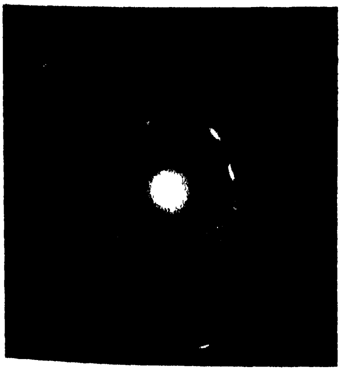

Fig. 13. Toluene

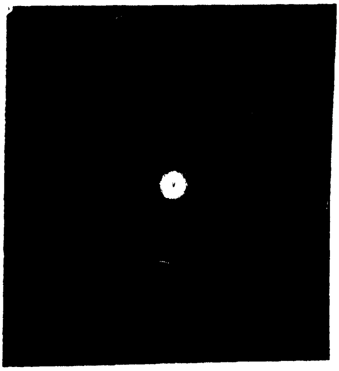

Fig. 16. Mesitylene

any definite meaning. Col. (4) gives the ratio between the values of cols. (2) and (3). We shall denote this ratio by k_1

TABLE 1.

Substance.	(1) θ_0	(2) $\dfrac{\lambda}{1{\cdot}63\ \mathrm{Sin}\ \theta_0/2}$ (A.U.)	(3) $1{\cdot}123\sqrt[3]{\dfrac{m}{d}}$ (A.U.)	(4) $(2)\div(3)=k_1$
Pentane	18·1°	6·00	6·49	·925
Hexane	18·3°	5·94	6·75	·881
Heptane	17·8°	6·10	7·01	·870
Octane	18·1°	6·00	7·26	·840
Oleic acid	18·3°	5·94	9·04	·663
Ether	19·2°	5·68	6·24	·910
Glycerine	19·8°	5·50	5·56	·988
Benzene	18·1°	6·00	5·94	1·01
Cyclo-hexane	17·0°	6·38	6·34	1·01
Phenol	18·1°	6·00	5·93	1·01
Toluene	16·5°	6·58	6·30	1·04
Aniline	17·6°	6·17	6·00	1·03
Water	27·3°	4·00	3·49	1·14

From an examination of the figures in table 1, it will be readily seen that though there is a sort of agreement between the values of cols. (2) and (3) in a few of the cases such as glycerine, benzene and cyclo-hexane, the disagreement generally observed is far too great to be missed even at first sight. Moreover, in the case of the aliphatic hydrocarbons, pentane to octane, there is a very interesting progressive decrease in the value of the ratio k_1 in col. (4). But by far the most striking case is that of oleic acid for which the mean molecular distance as obtained from Ehrenfest's formula is as low as 66% of the value calculated on the assumption of closest packing. While on the one hand, k_1 is less than unity for the hydrocarbons and oleic acid, it is greater than unity for toluene, phenol and water. Its value for the last-mentioned liquid is as high as 1·14, and would lead us to the impossible assumption that the molecules of this liquid are even more densely packed than in the closest packing arrangement. These results show conclusively that the arbitrary assumption of Keesom and Smedt about close-packing of molecules in liquids is untenable, and that the agreement obtained by them in the few cases they studied was merely accidental. We shall now use the method of Raman and Ramanathan in order to calculate the mean molecular distance from the diffraction data. These authors first calculate from the angular diameter of the principal halo the spacing of the diffracting planes which give rise to it, using for the purpose the well-known Bragg formula

$$\lambda_0 = \frac{\lambda}{2 \sin \theta_0/2}$$

If λ_0 be identified with the mean distance between neighbouring molecules, then we may write

$$a = \frac{}{2 \sin \theta_0/2} \tag{5}$$

which is of the same form as (4) except that the constant 1·63 in the denominator is replaced by 2. Raman and

Ramanathan do not make any special assumption as regards the distribution of molecules in the liquid, but on the other hand they attempt to obtain information about this distribution in any individual case from the experimental results themselves in the following way. For a fluid, liquid or gas, the mean distance a between neighbouring molecules is of the same order of magnitude as $n^{-\frac{1}{3}}$ where n is the number of molecules per unit of volume. We can therefore write

$$a=k\sqrt[3]{n=l}\quad\sqrt[3]{\frac{m}{d}} \qquad (6)$$

where m is the mass of a molecule of the fluid, d is the density of the fluid, and k is a constant. The value of k can be theoretically calculated for some simple cases. For example $k=\cdot 554$ for an ideal gas[1], unity for a regular cubical arrangement of molecules, and $2^{\frac{1}{6}}$ or 1·123 for the closest possible-packing.[2] In a liquid, the arrangement of the molecules must generally be intermediate in type between the absolutely chaotic distribution characteristic of an ideal gas and the regular arrangement characteristic of a crystal. In any case k cannot be more than 1·123 for the closest possible packing and must have a value somewhere between ·554 and 1·123. The problem has been discussed in a recent paper by Raman[3] who concludes that for a liquid, the value of k may range from ·8 to 1·0, according to the nature of the liquid and its condition as to temperature and pressure, etc. Definite information on this point in any particular case can be obtained from measurements of the X-ray diffraction-halo, by comparing the results obtained from equations (5) and (6) respectively. Table 2 sets forth the required data for the purpose.

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[1] Hertz, Math. Annalen 67, 1909, p. 387.

[2] Jean's Dynamical Theory of Gases, 3rd edition, p. 330.

[3] C. V. Raman, Phil. Mag., xlvii, April, 1924, p. 671.

TABLE 2.

Substance.	(1) θ_0	(2) $a = \frac{\lambda}{2 \sin \theta_0/2}$ (A. U.)	(3) $\sqrt[3]{\frac{m}{d}}$ (A. U.)	(4) Col. (2) ÷ Col. (3) = k.
Pentane ...	18·1°	4·90	5·77	·847
Hexane ...	18·3°	4·85	6·01	·808
Heptane ...	17·8°	4·97	6·24	·797
Octane ...	18·1°	4·90	6·47	·758
Oleic Acid ...	18·3°	4·85	8·05	·603
Ether	19·2°	4·63	5·56	·834
Glycerine ...	19·8°	4·49	4·95	·906
Benzene ...	18·1°	4·90	5·29	·926
Cyclo-hexane ...	17·0°	5·20	5·64	·924
Phenol ...	18·1°	4·90	5·23	·927
Toluene ...	16·5°	5·37	5·61	·957
Aniline ...	17·6°	5·03	5·34	·942
Water ...	27·3°	3·27	3·11	1·05
Butyric acid * ...	19·2°	4·63	5·35	·865

The way in which the value of k varies from liquid to liquid is indeed remarkable and gives us a novel insight into the nature of the liquid. How closely the molecular distribution follows the shape of the molecule as found by the chemist, is really striking. In the first place, there is a difference in this respect between the long-chain aliphatic molecules and the more symmetrical ring-formed molecules of the aromatic series. To illustrate this point, let us compare

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* Measurements for this liquid were obtained from a preliminary picture with a broader incident beam.

the values of *k* for the two liquids hexane (C_6H_{14}) and cyclo-hexane (C_6H_{12}), the molecules of which possess the same number of carbon atoms, and nearly the same molecular weight. The value of *k* for cyclo-hexane is nearly 15 per cent. higher than that for hexane, showing clearly that the molecules of the former are much more closely-packed than those of the latter. The elongated shape of the hexane molecules does not permit of such a close-packing as is possible in the case of the roundish molecules of cyclo-hexane, a lot of free space between the molecules remaining unoccupied in the former case. The difficulty of long molecules closely packing together is obvious, and can be realised by considering the analogous case of a number of long nails put together at random. The shape of the molecules is therefore naturally expected to have a profound influence on their packing.

The above conclusion is further supported by the fact that the values of *k* for benzene and its derivatives, phenol and aniline are, as should be expected, nearly the same as that for cyclo-hexane. A comparison of the hydrocarbons, pentane to octane puts the whole matter beyond doubt. With the progressive lengthening of the chain, there is also a progressive decrease in the value of *k*, showing clearly how increasingly difficult it is becoming for the molecules to pack themselves together as the chain gets more and more extended. The case of oleic acid is, however, the most remarkable of all. The chain has now become excessively long, consisting as it does of no less than 18 carbon atoms and the value of *k* too has become exceedingly low (·603) being not much above the value ·554 for an ideal gas with its perfectly chaotic distribution of molecules.

While, on the one hand, going up the series from pentane results in a steady diminution in the value of *k*, the reverse is, on the other hand, true when we examine shorter chain compounds than pentane. The higher values for glycerine and butyric acid may be cited as examples. The unusually high value (1·05) for water is due to its small and symmetrical molecules and indicates an arrangement nearly approximating to the hexagonal closest packing. This accords with the fact that powder photographs from ice [1] show a hexagonal close-packed arrangement and further that the specific volume for water is even a little less than that for ice.

An examination of the values of θ_0 for the first 5 liquids of table 2 brings out another interesting aspect of the question. It is remarkable how the size of the halo remains more or less unaltered although the length of the molecules undergoes an enormous increment, namely from 5 to 18 carbon atoms. It seems as though, so far as X-ray diffraction is concerned, the effective distance between the diffracting centres always remains the same, no matter how long the molecule becomes. This is very likely due to the fact that the probability of these long molecules lying end to end is very small, whereas the probability of their lying side by side is comparatively very large. To understand this clearly, let us suppose that two neighbouring molecules are placed horizontally, and that the second one lies vertically above the other. Now suppose this second molecule to be turned about a vertical axis passing through its middle. In all the positions which it occupies, its distance from the first molecule remains the same, namely, equal to the cross-section of the molecule. There are, thus, considerably more ways of arranging the molecules side by side than of arranging them end to end, and consequently it is the cross-section and not the length which would be effective in X-ray diffraction. Since this cross-section remains the same throughout, even though the length of the molecule is considerably increased, the constancy in size of the halo is obvious.

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[1] D.M. Dennison, Phys, Rev. 17, Series 2, 1921, p. 20.

5. *Relation of Diffuseness of Halo to Compressibility.*

According to the theory put forward by Raman and Ramanathan, the distribution of intensity in the scattered beam will depend upon a number of factors, namely, compressibility, temperature, etc. [see equn. (2)]. We can see in a general way how the compressibility comes in equn. (2). As is well known, according to Boltzmann's entropy-probability principle, the thermo-dynamic probability P of a particular configuration is related to its potential energy W by the following expression

$$P=exp\left(-\frac{N}{RT}W\right)$$

Now it is easily seen that when a group of molecules is pushed closer together, the distance between them is diminished and therefore also the distance between the successive layers which act as reflecting planes for the X-rays. The work necessary for this purpose will be proportional to the elastic forces that are operative and consequently inversely proportional to the compressibility. This would give β in the denominator in the index of e in the above expression for the probability of a certain spacing in the periodic distribution of matter and therefore also for the intensity of the scattered rays in the direction corresponding to this particular spacing or periodic distribution.

For the sake of convenience, we shall rewrite equn. (2) of these authors in the following form.

$$I=C_1 \text{ exp.}\left\{-\frac{1}{16}\,\frac{N}{RT\beta}\lambda_0{}^3\left(1-\frac{\text{Sin}^3\frac{\theta_0}{2}}{\text{Sin}^3\frac{\theta_1}{2}}\right)\right\},$$

where θ_0 is the angle corresponding to the principal halo, and θ_1 is any scattering angle. If we now plot I for various values of θ_1, or more accurately for values of $\frac{\theta_1}{\theta_0}$, we shall get a curve, the form of which will depend only on the magnitude of the term $\frac{N\lambda_0^3}{16RT\beta}$ in the exponential. It is obvious that the larger the value of this term, the sharper will be the maximum and *vice-versa.* A test of the general correctness of the above equation can, therefore, be made if we find the value of this term for a number of liquids so chosen as to give a sufficient range of variation of the term and examine the haloes in the light of these values. Let us denote this term by A for the convenience of further reference. Table 3 sets forth the values of A for nine of the liquids investigated in the present work. The other liquids are left out, because as we shall see later in sec. 7, in their cases another factor, namely, the structure of the molecule begins to be operative in diminishing the sharpness of the halo, and in some cases becomes so preponderant as to entirely mask the effect we are considering at present. As has already been mentioned in the last paragraph of sec. 3, this complication is most prominent in the case of the aromatic liquids, and for this reason, it has been considered proper to restrict the discussion of the influence of compressibility to the aliphati ccompounds, mostly hydrocarbons which do not show much complication due to this new factor. Benzene and aniline have, however, been included also on account of their comparatively simple molecular structure (see sec. 7). In addition to these, water will also be found in the list.

λ_0 in col. (2) is obtained directly from the measurement of θ_0 and is in fact taken from table 2. An attempt has been made to secure as large a range of compressibilities as possible, the actual variation extending from 257×10^{-12} for pentane to 25×10^{-12} for glycerine. A also has a correspondingly large variation, from ·70 to 6·53 and will further be found to be changing in the inverse order of compressibility, except for a discontinuity in the case of water where the small value of β is compensated for by the unusually small

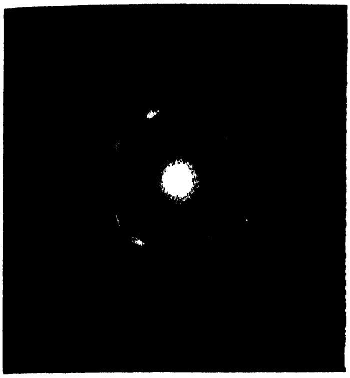

Fig. 17. O-Xylene

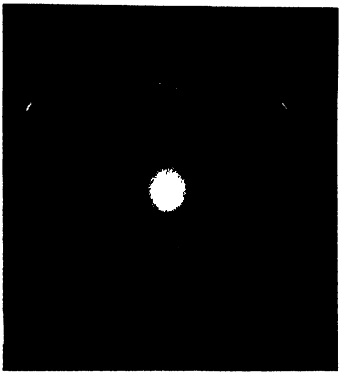

Fig. 20 O-n-toluene

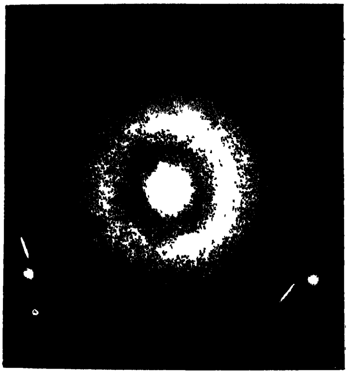

Fig. 18. M-Xylene

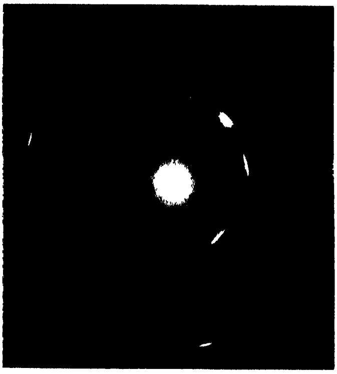

Fig. 21. M-n-toluene

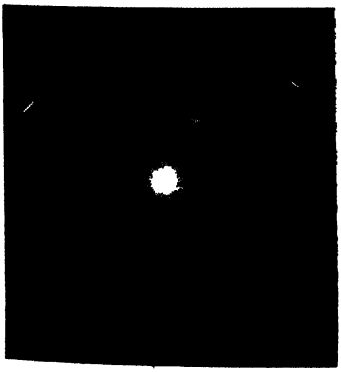

Fig. 19. P-xylene

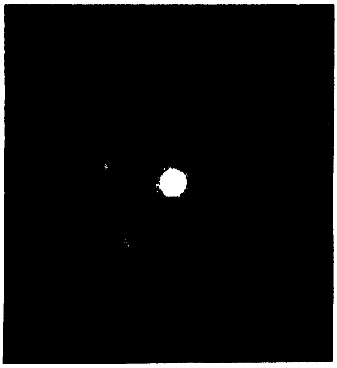

Fig. 22. P-n-toluene

value of λ_0^3, giving a fairly low value of A in spite of the low value of the compressibilty. The various substances are arranged in table 3 in the order of increasing A, and the corresponding photographs in Pls. XIV and XV are also arranged in the same order in order to facilitate comparison.

TABLE 3.

T=298° Abs.

Substance.	λ_0 (A. U.)	$\beta \times 10^{12}$ (at 25°C)	$\frac{1}{16}\frac{N\lambda_0^3}{RT\beta}$
Pentane	4·90	257	·70
Ether	4·63	182	·82
Water	3·27	45	[illegible]
Hexane	4·85	158	[illegible]
Heptane	4·97	134	[illegible]
Octane	4·90	121	[illegible]
Benzene	4·90	99	1·82
Aniline	5·03	45	4·33
Glycerine	4·49	25	5·53

The following points are clearly brought out by an examination of the photographs of these liquids, given in Pls. XIV and XV.

(1) *Pentane and ether.*—The first liquid in table 3, *viz.* pentane with the highest compressibility and the lowest value of A has really a very diffuse halo, more diffuse than that of any other liquid in the list with the exception of ether which comes second in this list. An explanation of this slight discrepancy probably lies in the importance of the molecular structure factor in this case (see sec. 7).

(2) *Water, hexane and heptane.*—These liquids come next to pentane and ether. Their haloes, though still diffuse, are a little sharper than the pentane halo. The minute difference between pentane on the one hand and hexane and heptane on the other, is better seen from a comparison of the original negatives themselves. But a close examination of even the prints published makes this difference quite clear.

(3) *Octane and benzene.*—The small changes that have been gradually occurring at each step from pentane to heptane have now sufficiently accumulated. The haloes for these two liquids are unmistakably sharper than the previous haloes. The difference is now too great to be missed even at first sight.

(4) *Aniline and glycerine.*—These possess the lowest compressibility, and their haloes are remarkably sharp. They are, in fact, the sharpest of all.

The way in which the sharpness of the halo is found closely to follow the changes in compressibility or, more accurately, changes in the value of A is quite remarkable and clearly signifies that at least for simpler molecular structures, the theory of Raman and Ramanathan has a basis of truth.

In order to eliminate the molecular-structure factor altogether, the best plan, however, will be to study the same liquid at different temperatures and see if with rise of temperature and consequently increase of both τ and β, the halo also broadens. From the numerous cases discussed in this section, however, and from the fact all the haloes except one nicely fit in the places assigned to them by the value of A, there is hardly any doubt that the effect observed is genuinely one due to compressibility and is not disturbed by any appreciable degree in these cases by the other factor. Ether which is the only exception falls just a little outside the scheme, being actually found first from the point of view of diffuseness of the halo instead of being second as the theory indicates.

6. *Scattering at small angles.*

An examination of the region inside the halo in the original negatives shows a certain amount of variety in the intensity of scattering at these small angles. A general statement that the intensity at small angles is small or large is clearly shown to be without meaning. Whether this scattering is small or large depends entirely on the nature of the particular liquid in question.

It is true that it is impossible to make any quantitative visual estimates of the amount of relative blackening. By making photometric measurements alone, is it possible to decide this question satisfactorily. Even the visual observations, however, do enable us undoubtedly to perceive some broad differences. We can, for example, divide the liquids into two broad classes, the liquids of one class showing a fair amount of darkening in the inner region (in the negatives), while on the other hand this region is unmistakably clearer in the case of the liquids of the other class. The comparison becomes easier and more certain if two or more negatives are put side by side. The actual observations show that liquids benzene, cyclo-hexane, aniline, phenol, toluene and glycerine belong to the class showing very little scattering at small angles, while, on the other hand, liquids like pentane, hexane, heptane, octane, oleic acid, etc. belong to the other class and show comparatively much more scattering in this region. To illustrate our point, the examples of hexane and cyclo-hexane may be mentioned. The difference between the negatives of these two liquids is indeed striking. Whereas cyclo-hexane shows an intense and sharply-defined halo with a very clear space within, hexane, on the other hand, shows a less intense and relatively more diffuse halo, the inner margin of which is not sharply terminated but extends almost up to the direction of the incident X-rays.

It thus appears that liquids like cyclo-hexane* aniline, phenol, benzene, etc., with rather symmetrical molecules and low values of compressibility scatter much less at small angles than liquids like pentane, hexane, heptane, etc., having less symmetrical molecules and higher compressibility.

The scattering of X-rays at small angles arising from these two factors, *viz.*, compressibility and shape of the molecule may be considered analogous to the "density" and "orientation" scattering in the optical case.[1] It should be remembered, however, that while the "orientation" scattering in the optical case arises from the optical *anisotropy* of the molecule, the "orientation scattering" of X-rays is connected with the deviation of the geometrical form of the molecule from spherical symmetry. This is very clear by a comparison of the effects observed with hexane, cyclo-hexane and benzene. Optically, hexane and cyclo-hexane have a very small orientation scattering and differ in this respect very much from benzene, while in the X-ray region cyclo-hexane and benzene have a small orientation scattering and differ widely from hexane.

7. *Influence of Molecular Form and Structure.*

As has been mentioned already in sec. 3, the benzene derivatives studied give very striking results. A glance at Plates XVI and XVII will show at once what a remarkable variety we have there in the structure of the halo. Starting with the simple sharp halo for benzene (Pl. XV), we have in so many cases haloes nearly three times as wide, and in three cases the wide halo develops a further interesting structure and is broken up, as it were, into two clear rings with a dark region between. There is, however, a system underlying all this interesting variety, as will be clear from the discussion that follows of the way in which the halo is found to be modified more and more as the complexity of the molecule increases. Not only does the structure of the principal halo alter when we pass from one benzene derivative to another with a different molecular formula, but even the minor differences in the spatial arrangement of atoms or groups constituting different isomeric molecules are also found to be clearly reflected in the structures of their haloes.

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* Data for the compressibility of cyclo-hexane are not available.

[1] C. V. Raman and K. S. Rao, Phil. Mag. 45, 1923, p. 625.

The various photographs will all be found in Pls. XVI and XVII with the exception of those for benzene and aniline which will be found in Pl. XV. The figures in the plates are arranged nearly in the order of increasing complexity of the liquid molecule. Liquids with molecules possessing only a single substitution group at one corner of the benzene ring are put first. Then we have molecules with two substitutions. In order to be able to put the three xylenes and the three nitrotoluenes in the same plate, mesitlyene with three substitution groups has been put before the xylenes, in the previous plate. Even amongst liquids possessing the same number of substitution groups, those having lighter group or groups have been placed before those with heavier groups.

Even from a cursory examination of the various figures, the conclusion is obvious that there is a progressive change in the halo as we pass from benzene to its more and more complex derivatives. That these changes cannot possibly be due to variations in compressibility is at once made evident by a reference to the compressibility-data for the various liquids in question. It will be found that the figures range from 99×10^{-12} for benzene to 45×10^{-12} for aniline. The data for the three nitrotoluenes are not available, but will perhaps not be far different from the value (53×10^{-12}) for nitrobenzene. As will be clear from the discussion in sec. 5, the influence of compressibility which is in all cases small is marked only for high values of this constant, say above

100×10^{-12}. For lower values, this influence is much less marked. Anyhow, it will be quite clear from sec. 5 that the modifications in the halo we are considering at present are of a much bigger order than any effects due to compressibility.

We shall now arrange the results obtained in a suitable form in order to be able to understand the phenomenon more clearly.

(1) *Benzene* (C_6H_6) *and cyclo-hexane* (C_6H_{12}).—Benzene is one of the most interesting liquids in organic chemistry. Its molecule is ring-formed and possesses a more or less uniform and symmetrical structure, there being the same CH group at each corner of the regular hexagon. This would naturally mean a more or less uniform distribution of the diffracting electrons. It will be seen that the halo for benzene (fig. 7) is fairly sharp. This has been shown also to be in accord with the moderate value of its compressibility. The same arguments apply to cyclo-hexane also, and the strikingly well-defined halo for this liquid is thus explained. The fact that this halo is sharper even than the one for benzene suggests that the cyclo-hexane ring is even more symmetrical than the benzene ring. It is also possible, however, that this may be due to smaller value of the compressibility for this liquid. Unfortunately, however, compressibility data for cyclo-hexane are not available and we are consequently not in a position to decide which one factor is operative here more than the other.

(2) *Phenol* ($C_6H_5{\cdot}OH$); *aniline* ($C_6H_5{\cdot}NH_2$) *and toluene* ($C_6H_5{\cdot}CH_3$).—These are the three simplest substitution products of benzene. The symmetry of the molecule is in these cases disturbed by the loading of one corner of the benzene ring by an OH, a NH_2 and a CH_3 group respectively. The asymmetry caused, however, is small, as can be seen from the fact that the number of electrons in these additional groups is only 9, 8 and 9 respectively, numbers small in comparison to the total number 41 in the benzene group. It will be seen

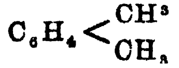
from figs. 12, 8 and 13 that the phenol and toluene haloes do not differ much from benzene in their structure. The aniline halo on the other hand is quite sharp. This is evidently due to the very low value of compressibility for this liquid. There is a further interesting detail which the aniline picture shows, *viz.*, a faint illumination extending to a few degrees outside the halo. Benzene, phenol and toluene also show this effect, though to a less extent.

It thus seems that the small asymmetry in the molecules of these three liquids makes only a small impression on the nature of their haloes.

(3) *Ethyl-benzene* ($C_6H_5 \cdot C_2H_5$) *and nitro-benzene*($C_6H_5 \cdot NO_2$).—Fig. 14 corresponds to ethyl-benzene. Here the C_2H_5 group possesses 17 electrons and is heavier than in the previous cases. The asymmetry of the molecule has therefore increased and the halo too has undergone an unmistakable change. It is distinctly broader than the previous haloes.

Fig. 15 for nitro-benzene (NO_2-23 electrons) is indeed remarkable. The halo is now nearly three times as broad as the benzene halo. This profound change is obviously due to the highly unsymmetrical form of the molecule due to the big NO_2 group.

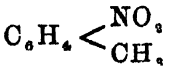
(4) *Ortho, meta and para-xylenes.*—These xylenes are isomers with the general formula



$$C_6H_4 < \begin{matrix} CH^3 \\ CH_3 \end{matrix}$$

and with a molecular weight equal to that of ethyl-benzene. The relative positions of the two CH_3 groups in the three isomers are well-known. In ortho, they are at two adjacent corners, in meta at alternate, and in para at opposite corners. Now it will be seen that the halo for o-xylene (Fig. 17) is not much different from that for ethyl-benzene. This is exactly what one might expect also, for two CH_3 groups at two adjacent corners should not be much different from a C_2H_5 group at one, from the point of view of X-ray scattering. If, however, they are placed at alternate corners as in m-xylene, the shape of the molecule is modified considerably and can no longer be regarded as equivalent to ethyl-benzene. Fig. 18 shows this clearly. The halo is extended considerably on the outside, and in fact, shows a marked discontinuity in the middle, making it look very likely that it is a superposition of two rings not sufficiently resolved. Curiously enough, para-xylene again shows a similarity to ethyl-benzene and ortho-xylene and differs considerably from meta-xylene. This may be a consequence of the fact that the molecule has now become more symmetrical on account of the equal loading at two opposite corners.

(5) *Ortho, meta and para-nitrotoluenes.*—These isomers have the formula



$$C_6H_4<\begin{matrix}NO_2\\CH_3\end{matrix}$$

As in the xylenes, the two groups, CH_3 and NO_2 are at adjacent corners in ortho, at alternate corners in meta, and at opposite corners in the para compound. A glance at Figs. 20-22 will at once show the remarkable development that has now taken place in the diffraction halo. Instead of the single sharp halo of benzene, or the wide halo for nitrobenzene or even the imperfectly resolved halo for m-xylene, we now have in the case of ortho and meta-nitrotoluenes, two rings clearly resolved. It is interesting to note, however, that in spite of this new development, the total width of the halo including both the rings is nearly the same as that for nitrobenzene. It is also remarkable that one of the two rings is smaller and the other bigger than the simple benzene ring.

Here again, as in the case of the xylenes, the ortho and meta compounds differ strikingly from each other, the distribution of intensity inside the halo being different in the two cases. In the ortho, the inner ring is much brighter than the outer, while in the other case, the reverse is true. Further, the halo for the meta has shrunk to a slightly smaller size also.

Like para-xylene, para-nitro-toluene also seems to stand apart. But its apparently anomalous behaviour can be understood if we follow up the change that has taken place from the ortho to the meta a step further. With a further diminution in the brightness of the inner ring and a proportionate increase in that of the outer, along with a simultaneous shrinking of the whole to a still smaller size, we shall get a halo very much like fig. 22. There is, however, another way of looking at the matter. A comparison of figs. 15 and 22 shows the resemblance between nitrobenzene and this compound, and the halo of the latter can be regarded as a modification of the former owing to the presence of an extra CH_3 group at the opposite corner to the NO_2 group. On account of the peculiar situation of the CH_3 group at a great distance from the NO_2 group, for purposes of X-ray diffraction, para-nitro-toluene can be regarded as related to toluene in much the same way as nitro-benzene is related to benzene, and therefore the similarity of the haloes of these two nitro-compounds is natural. These considerations, however, do not apply to the ortho and meta on account of the greater proximity of the two groups and their unsymmetrical positions.

(6) *Mesitylene.*—The molecule of this liquid is derived from that of benzene by substitution of a CH_3 group at the three alternate corners (1 : 3 : 5) of the ring. The halo for this liquid (fig. 16) again consists of two clear rings similar to ortho and meto-nitrotoluenes, the two rings being equally bright in this case. It may be considered to be a development of the imperfectly resolved halo of meta-xylene owing to the addition of an extra CH_3 group to the molecule of this liquid.

The results of the comparative study set out above clearly show the systematic way in which the principal halo of the liquid pattern is influenced by the internal structure of the molecule, and are very instructive. As yet, however, it is not quite clear why the shape and constitution of the molecule bring about the remarkable changes observed. Whether the asymmetry of the molecule directly affects its scattering power in different directions, or whether it is effective only in an indirect way in so far as it may influence the arrangement of the molecules in the mass of the liquid, remains yet to be settled. Further experiments are in progress which may lead to a clear understanding of these remarkable phenomena.

In conclusion, the writer has great pleasure in expressing his best thanks to Prof. C. V. Raman, F.R.S., who suggested the work and under whose guidance it was carried out at the laboratory of the Indian Association for the Cultivation of Science, Calcutta.

CALCUTTA,
The 7th April, 1927.

The Molecular Scattering of Light in Aqueous Solutions

PART II

BY

S. VENKATESWARAN.

The experimental results on the molecular scattering of light in aqueous solutions of some inorganic acids were given in the first paper.[1] The theory of Raman and Ramanathan[2] for light-scattering in binary liquid mixtures was discussed and it was shown that as far as light scattering was concerned, solutions of HCl, HNO_3 and H_2SO_4 behaved like single liquids and not as binary mixtures. The contribution to the intensity of the scattered light from concentration fluctuations was found to be negligible in comparison to the density scattering. It would therefore be interesting to study the behaviour of solutions of some organic acids with regard to light-scattering and find out whether they behave like the solutions of inorganic acids studied in the first paper or like true binary mixtures contemplated in the theory. With this object the light-scattering of aqueous solutions of acetic, propionic and butyric acids was studied and the results are set forth in this paper.

Experimental.

The acids used were all Kahlbaum's pure chemicals and were obtained optically dust free by repeated slow distillations in vacuo in double-bulbs of the pattern used by Martin,[3]

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[1] S. Venkateswaran, Indian Journal of Physics, Vol. I, part 2, 1926-7, p. 235.

[2] C. V. Raman and K. R. Ramanathan, Phil. Mag. [vi], 45, 213, 1923.

[3] W. H. Martin, Journ. Phys. Chem., 26, 75, 1922.

Krishnan[1] and other investigators. The experimental details were exactly the same as those mentioned in the previous paper. Polarisation measurements of the transversely scattered light were made by a double image prism and nicol. The two images of the prism were brought in a line and by rotating the nicol, two positions could be found in which the images appeared of equal intensity. If 2 θ be the angle between these positions of the nicol, then $r = \tan^2 \theta$ where r is the ratio of the two components. As in the previous case the intensities of the scattered light in dilute solutions were compared directly with that of dust-free distilled water, using an Abney rotating sector photometer for the purpose. In the case of solutions where the intensities of the scattered light were much greater than that of water, the comparison was made in two or three stages, using some intermediate standards. For example, 27·6 per cent. butyric acid at 2°C. scatters more than 100 times water. The intensity in this case was compared with that of the light scattered by a block of colourless Jena glass. The glass was then compared with dust free ether, which in its turn was finally measured with respect to water.

As in the case of the acids described in the first paper, the bulbs were cut open after the depolarisation and intensity measurements were over and the strengths of the acids were determined by titration with standard caustic soda solution.

Results.

The results of the measurements on the imperfection of polarisation of the scattered light are given in Table I. The ratio of the weaker component, having its vibrations parallel to the incident beam, to the stronger component having its vibrations perpendicular to the same, is expressed as a percentage. Table II gives the observed intensities of the scattered light in terms of the light scattered by dust-free water and also values calculated from the theoretical expression for the density scattering. Table III gives the values for the concentration scattering for propionic and butyric acids, obtained by difference between the total intensity (observed value) and the part due to density scattering.

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[1] K. S. Krishnan, Phil. Mag., 50, 697, 1925.

TABLE I.

Depolarisation of the transversely scattered light.

White incident light (unpolarised).

Strength of acid per cent.	$\frac{\text{Weak component}}{\text{Strong component}} \times 100$	
	2°C.	30°C.
Acetic acid.		
12·85	……	19·8
34·57	……	30·7
52·90	……	38·1
80·63	……	44·3
100·00	……	46·5
Propionic acid.		
10·21	……	16·6
31·23	……	20·9
53·50	……	24·0
81·40	……	32·0
100·00	……	41·2
Butyric acid.		
27·60	1·3	2·1
46·06	1·9	4·3
77·38	26·4	26·0
100·00	40·9	41·0
*Water	……	9·6

* Value obtained by Krishnan.

TABLE II.

Intensity of the transversely scattered light.

White incident light (unpolarised).

Strength of acid per cent.	Intensity relative to water = 1.		
	Density scattering Ω_1 (calculated.)	Observed value at 2°C.	Observed value at 30°C.
Acetic acid.			
12·85	1·43	......	1·30
34·57	2·02	......	2·12
52·90	2·93	......	2·90
80·63	5·10	......	4·75
100·00	7·75	......	7·50
Propionic acid.			
10·21	1·27	......	1·44
31·26	1·72	......	1·82
53·50	2·33	......	2·64
81·40	4·10	......	4·30
100·00	6·78	......	6·48
Butyric acid.			
27·60	1·11	110·0	27·9
46·06	1·47	59·5	19·4
7·783	3·37	5·4	3·6
100·00	7·52	6·0	6·3

Discussion of Results.

(*i*) **Intensity.**—The intensity of the transversely scattered light is given by the theoretical expression*

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* C. V. Raman and K. R. Ramanathan, Phil. Mag., 45, 213, 1923.

$$I = (\Omega_1 + \Omega_2)\,\frac{6\,(1+r)}{6-7r} \quad \text{where} \quad \Omega_1 = \pi^2\,\frac{R\,T\,\beta\,(\epsilon-1)^2\,(\epsilon+2)^2}{18\,N\,\lambda^4}$$

denotes the part arising from density fluctuations, $\Omega_2 = \pi^2 \dfrac{M_2\,(\delta\epsilon / \delta\ k)^2}{N\,\lambda^4\,m_1\,\delta \log p_2 / \delta k}$ represents the part arising from the concentration fluctuations and $\dfrac{6\,(1+r)}{6-7r}$ is the multiplying factor applied to both to take into account the anisotropy of the medium.

For calculating Ω_1 we require to know the values of β, the isothermal compressibility, and the refractive index of the mixture. In all cases the refractive index for the F line was taken for the calculation and reduced to the temperature of the experiment by using Lorentz-Mosotti formula. As data regarding the refractive index for the solutions of the acids were not available, they were calculated from the formula for the refractive index of mixtures,

$$\frac{\epsilon-1}{(\epsilon+2)\rho} = \frac{\epsilon_1-1}{(\epsilon_1+2)\rho_1}\,x + \frac{\epsilon_2-1}{(\epsilon_2+2)\rho_2}\,(1-x)$$

where ϵ_1, ρ_1 and ϵ_2, ρ_2 refer to the two components of the mixture.

Regarding the isothermal compressibility for acetic acid, Tyrer's[1] value was used for 100 per cent. acid. For other concentrations β was calculated by extrapolation from the values at higher pressures obtained by Drucker.[2] In the case of propionic and butyric acids and their solutions, data for the isothermal compressibilities were not available. The adiabatic compressibilities of these liquids for a change of pressure from two atmospheres to one atmosphere, were determined for the purpose. β can be calculated from the adiabatic compressibility, α, with the help of the relation

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[1] D. Tyrer, Journ. Chem. Soc., London, 105, 2534, 1914.

[2] Cohen and Schut, Piezochemie, Leipzig, 1919, p. 127.

$$\beta = \alpha + \frac{T\left(\frac{dv}{dt}\right)^2}{J.\, v.\, c_p},$$

where the different letters have their usual significance. The values of c_p and $\frac{dv}{dt}$ were available for pure propionic and butyric acids only, and β was calculated for these two acids from the above expression. For acids of other concentrations, β was estimated with the help of the curves for α and β for acetic acid solutions.

To calculate the concentration scattering, Ω_2, we require to know the partial vapour pressure p_2 of one of the components. As the necessary data are not available for the solutions of any of the acids studied in this paper, the values of Ω_2 could not be calculated.

Columns 2 and 4 in Table II give the calculated values of Ω_1 and the observed values for the intensities of the scattered light. A comparison of these two sets of values is very interesting. In the case of acetic acid there is a close agreement between the observed values, and the calculated values of Ω_1. This shows that the contribution to the total intensity due to concentration fluctuations, *viz.*, Ω_2, is very small. With propionic acid the difference between the observed value and the value of Ω_1 becomes appreciable, thus clearly indicating the existence of concentration scattering (see Table III). However, the values of Ω_2 are still small in comparison with Ω_1. But when we come to butyric acid, the values of Ω_2 become very large and indicate clearly the relative importance of density and concentration scatterings as seen from the following table.

TABLE III.

Strength of acid %	Intensity relative to water = 1		
	Observed value. I	Density scattering Ω_1	Concentration scattering (Ω_2). I—Ω_1
Propionic acid.			
10·21	1·44	1·27	0·17
31·26	1·82	1·72	0·10
53·50	2·64	2·33	0·31
81·40	4·30	4·10	0·20
Butyric acid.			
27·60	110·0	1·11	108·9
46·06	59·5	1·47	58·03
77·33	5·4	3·37	2·03

The intensities of the scattered light in butyric acid solutions show the critical opalescence phenomenon. Faucon* has studied the mutual solubilities of butyric acid and water at low temperatures and has shown that above —3·8°C. the two liquids are completely miscible. It is well known that such mixtures exhibit a marked opalescence near the critical solution temperature. In the immediate neighbourhood of the critical point, the partial vapour pressures alter very little with the composition of the mixture and hence the values of Ω_2 become very large in comparison with Ω_1. In fact, in the original expression for critical opalescence obtained by Einstein, the term for density scattering (Ω_1) is entirely neglected. As we go away from the critical point, Ω_2 gradually decreases. These facts are completely borne out by the results obtained with butyric acid solutions. As seen from Tables II and III, the values of Ω_2 are very large even at temperatures far removed from the critical solution temperature. It is seen that Ω_2 attains a maximum value near the critical point. It would be of great interest if the value for Ω_2 could be calculated from the theoretical expression, for comparison with the above values, but the necessary data are not available.

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* Ann. chim. phys., 19, 119, 1910.

(*ii*) Depolarisation.—The imperfection of polarisation of the light scattered by pure acetic acid is larger than with propionic or butyric acids. For the same molar concentrations the values of the depolarisation factor are higher in acetic acid solutions than those in the other two acids. The effect of concentration on the imperfection of polarisation is interesting in the case of butyric acid solutions. As we approach the critical point the scattered light becomes almost completely polarised, as is evident from the small values of r in the Table. Owing, however, to the enormous intensities of the scattered light, there is a large secondary scattering throughout the volume of the liquid, which is much less polarised than the primarily scattered light. It would be difficult to say whether the small imperfection that is actually observed is genuine or is due to the extraneous influence of this secondary scattering.

Summary.

The investigation on the molecular scattering of light in aqueous solutions has been extended to acetic, propionic and butyric acids. Unlike the solutions of the strong acids discussed in the previous part, these fatty acids show an appreciable concentration scattering which is characteristic of mixtures, its magnitude increasing rapidly as we proceed from acetic to butyric acid. With butyric acid solutions whose critical solution temperature is at —3°·8C. the variation of the intensity and depolarisation of the scattered light as we proceed towards the critical point, are in complete accord with theory.

In conclusion the author desires to express his best thanks to Prof. C. V. Raman, F.R.S., under whose guidance the work was carried out.

CHEMICAL LABORATORY,
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Arc Spectrum of Copper

BY

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The arc spectrum of copper which defied attempts at complete classification for the past thirty years has now been analysed, thanks to the labours of Shenstone,[1] Beals,[2] Sommer[3] and others. The writer had also been engaged for sometime past in this investigation and had arrived at results of almost identical nature to those of the above mentioned authors. The complete spectrum has so well been described by Shenstone and Sommer that it seems needless to give the details extensively. The present communication will be in the nature of a review of the subject in brief, giving out the author's own interpretation where he happens to differ from these workers.

The extraordinary complexity of the spectrum was evident from the large number of lines that were definitely known to be arc lines, and remained outside the scheme of ordinary series relationships. From older ideas it was found impossible to account for the presence of other lines except those which belonged to the doublet systems. Their number was only thirty while the spectrum showed no less than 450 lines between the red and the extreme ultraviolet region. It is only in the light of the theory of complex spectra, as given

[1] Shenstone, Phys. Rev., Vol. 27 (1926), p. 511.

[2] Beals, Proc. Roy. Soc., Vol. III (1926), p. 168.

[3] Sommer, Zs. f. Phys., Vol. 39 (1926), p. 711.

out recently by Hund,[1] and others, that a pictorial view of the production of terms as actually exists in the spectrum of copper, is presented to the investigator.

Russell and Saunders[2] suggested that the character of the spectral terms of an atom is given not by the quantum-characteristics of the last electron, but by quantum numbers which arise from a synthesis of the orbits of the individual electrons which constitute the last shell. Pauli[3] assumed that the fundamental orbits of the individual electrons are of the doubtlet type, like that of alkalies, and their nature is to be determined from the position of the electrons in the Stoner[4] scheme. He was able to work out the rules of synthesis in the case of the alkaline earths, and was able to explain the occurrence of only ${}^1S_0$—term, and the absence of ${}^3S_1$—term in the fundamental state. The rules were further extended by Heisenberg.[5] Hund[6] applied these rules for calculating the fundamental terms in the transitional group, Sc. to Cu. Prof. M. N. Saha[7] has proposed a scheme for representing the electronic arrangement in atoms, which gives an extremely realistic picture of the structures of the atoms, as well as of electron transitions leading to the production of spectral terms. Let us write out the structure-diagram of copper :

K_1 2						
	L_1 2	L_2 6				
		M_1 2	M_2 6	M_3 10		
			N_1 1	N_2	N_3	N_4
				O_1	O_2	O_3

Hund, Zs. f. Phys., Vol. 33 (1925), p. 841.
Russell and Saunders, Astrophys. J., Vol. 61 (1925), p. 38.
Pauli, Zs. f. Phys., Vol. 31 (1925), p. 765.
Stoner, Phil. Mag., Vol. 48 (1924), p. 719.
Heisenberg, Zs. f. Phys., Vol. 32 (1925), p. 841.
Hund, Zs. f. Phys., Vol. 33 (1925), p. 345.
Saha, Phil. Mag. (1927).

In the normal state the composition of the outer shell is given by $10M_8N_1$ (10 electrons in M_8 and one in N_1). Keeping 10 electrons in M_8 if we allow the other electron to run through the levels N_2N_3...... O_1O_2.........etc., we get the regular P, D,......sequence of the doublet spectrum of copper. Table I gives the regular terms in copper and the electron configurations from which they are derived :—

TABLE I.

Electron Configuration.	Terms.	Term Values.
$10M_3N_1$	1^2S_1	62308·0
$10M_3O_1$	2^2S_1	19171·1
$10M_3P_1$	3^2S_1	9459·5
$10M_3Q_1$	4^2S_1	5636·7
$10M_3N_2$	$1^2P_{1,2}$	31772·8, 31524·4
$10M_3N_3$	$1^2D_{2,3}$	12372·8, 12365·9
$10M_3O_3$	$2^2D_{2,3}$	6920·8, 6917·1
$10M_3P_3$	$3^2D_{2,3}$	4415·5, 4413·4
$10M_3N_4$	$1^2F_{3,4}$	6880·0

Let us now turn to the anomalous terms : $9M_82N_1$ gives us ^2D the inverted doublet terms 51105·5 and 49062·6, the natures of which were first established by Zeeman effect investigations of Runge[1] and Paschen, and later on by Werner and Ruark. The large value of these terms which correspond to the metastable state of the atom is to be expected from our diagram. The energy of the electron in the same vertical column is of the same order of value, though each succeeding term is shorter than the previous. Keeping 9 electrons in M_8

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[1] Quoted by Lütig, Ann. d. Phys., v. 38 (1912), p. 31.

and one in N_1 if we allow the other electron to run through all the higher available levels, we get all the terms discovered by Shenstone and Sommer. All these terms are given subsequently.

Combinatory Properties of the terms.

We can easily work out from the above diagram the combinatory properties of the terms. The rule is that if we can get from a combination (*a*) to another combination (*b*) by shifting the electron either horizontally or vertically or both together, an odd number of times then all terms arising from (*a*) will be capable of combining with all terms arising from (*b*), provided the selection principle for the inner quantum number is obeyed. If two electrons are to be shifted in getting from (*a*) to (*b*) the number of transitions of each, added together, ought to be odd. Also all terms arising from a particular combination will have identical combinatory powers.

$9M_3$ N_1 N_2 Combination

$9M_3$ gives ${}^2D$

N_1+N_2 gives ${}^3P$ ${}^1P$

The combination of ${}^2D$ with ${}^3P$ and ${}^1P$ gives us the following terms :

$$(a)\ {}^2D+{}^3P \text{ gives } \begin{cases} {}^4F & {}^4\overline{D} & {}^4P \\ {}^2F & {}^2\overline{D} & {}^2P \end{cases}$$

$$(b)\ {}^2D+{}^1P \text{ gives } \quad {}^2F \quad {}^2\overline{D} \quad {}^2P$$

Now Hund has laid down a general rule that of the terms arising from the same configuration those with the highest azimuthal quantum numbers are the deepest. It is therefore expected that the terms of combination (*a*) will be deeper than those of the combination (*b*), and will also combine more strongly with other terms. It will also be noted that the D's in the present case have been 'barred.' This follows immediately from the fact that to get to the configuration $9M_3N_1N_2$ from $9M_32N_1$ we have only to shift an electron horizontally from N_1 to N_2, and therefore the terms in the two cases will combine with each other easily. Consequently the D-terms of the present case have been 'barred' to enable them to combine with other D-terms. All these terms were predicted by Hund. The quarter terms were obtained by Beals from Zeeman effect data, and Shenstone independently, and later on confirmed by Sommer. We give below the values of the terms:

$9M_3 \; N_1 \; N_2$

$^4F_2 = 20005{\cdot}5$ $^4\overline{D}_1 = 17392{\cdot}2$ $^4P_1 = 21364{\cdot}3$

$^4F_3 = 20745{\cdot}2$ $^4\overline{D}_2 = 17763{\cdot}9$ $^4P_2 = 22194{\cdot}1$

$^4F_4 = 21154{\cdot}8$ $^4\overline{D}_3 = 17901{\cdot}8$ $^4P_3 = 23289{\cdot}4$

$^4F_5 = 21399{\cdot}0$ $^4\overline{D}_4 = 18794{\cdot}2$

$^2F_3 = 18581{\cdot}9$ $^2\overline{D}_2 = 16135{\cdot}2$ $^2P_1 = 16487{\cdot}1$

$^2F_4 = 17345{\cdot}1$ $^2\overline{D}_3 = 15709{\cdot}8$ $^4P_2 = 16428{\cdot}8$

The other set of $^2F \; ^2\overline{D} \; ^2P$ terms to be expected from this combination has not yet been unambiguously identified. Shenstone thinks that they may be present amongst some of the small terms ranging about the value 6000, and combining with the doublet D-terms of the combination $9M_32N_1$. The precise investigation of these terms cannot be undertaken as the combinations with ^2S will all lie beyond the range of quartz spectrograph, and the existing data do not seem to be sufficiently trustworthy. Nothing definite can be said, but it is probable these small terms may as well originate from the combination

$8M_32N_1N_2$ which gives rise to

$^4\overline{G}$ ^4F $^4\overline{D}$

$^2\overline{G}$ ^2F $^2\overline{D}$

These terms will strongly combine with the inverted ^2D terms because the transition from M_3 to N_2 is expected to be strong. It is for this reason also that G and D terms in this case will be barred. The terms obtained in this way are identified as follows:

$8M_3 2N_1 N_2$

$^4\overline{G}_3 = 6995 \cdot 0$	$^4F_2 = 7280 \cdot 3$	$^4\overline{D}_1 = 4888 \cdot 9$
$^4\overline{G}_4 =$?	$^4F_3 = 7523 \cdot 9$	$^4\overline{D}_2 = 5656 \cdot 4$
$^4\overline{G}_5 =$?	$^4F_4 =$?	$^4\overline{D}_3 = 5964 \cdot 1$
$^4\overline{G}_6 =$?	$^4F_5 =$?	$^4\overline{D}_4 =$?
$^2\overline{G}_4 =$?	$^2F_3 = 4188 \cdot 1$	$^2\overline{D}_2 = 3617 \cdot 2$ (?)
$^2\overline{G}_5 =$?	$^2F_4 = 6278 \cdot 2$	$^2\overline{D}_3 = 3772 \cdot 1$

Since these small terms have been derived from the combinations with ^2D-terms it has not yet been found possible to isolate the terms with inner quantum numbers higher than 3. The presence of this combination may also be expected from analogy with the spectrum of nickel, where the same number of eletrons come into play as in Cu^+. Now the fundamental terms of nickel arise from combinations $8M_3 2N_1$ and $9M_3 N_1$, and if the spectrum of Cu^+ has a similar constitution then the existence of the $8M_3 2N_1 N_2$ combination would be rendered more probable. A thorough investigation of the spectrum of Cu^+ will decide the point one way or the other.

Origin of Negative Terms.

There are a large number of negative terms obtained by Beals, Shenstone, Sommer and the present writer which give rise to some very strong lines in the spectrum of copper. It is very easy to work out the origin from which these terms arise for they clearly point to the simultaneous displacement of two electrons from the normal levels.

The idea of simultaneous displacement of two electrons was put forward by Wentzel[1] and independently by Russell and Saunders,[2] who were led to this conception from a study of the limit of $^3\overline{P}$ series in the spectrum of calcium which comes out to be negative. The presence of negative terms means that more energy is required to develop these terms than is required for ionising the element. In order that this may happen, without ionising the atom, the energy must be divided up between two electrons, each one of which rises to some higher orbit, and then falls back to its normal position, with the emission of energy corresponding to the transition. So far the idea is the same as applied to the production of regular series lines. But there is one essential difference in this case brought about by the simultaneity of two jumps in the same atom. The two energies from the displacement of two electrons do not become available separately, but are added together and come out as a single monochromatic radiation. The higher Rydberg sequence to the fundamental anomalous terms are formed when one electron remains fixed in the displaced level and the other electron runs through the successive higher orbits corresponding to the same azimuthal quantum number. The meaning of these negative terms will be made clearer by considering the following concrete instance.

Let us take the structure diagram of Cu, and consider the states.

$9M_3 2N_1$	$9M_3 N_1 O_1$	$9M_3 N_1 P_1$	$9M_3 N_1 Q_1$
1^2D	1^4D 2^2D	2^4D 3^2D	3^4D 4^2D

which are obtained by one electron in N_1 and shifting the other through the diagonal levels O_1 P_1 Q_3.........We shall get ^4D and ^2D-terms; and the higher ^2D-terms will form a Rydberg sequence with the fundamental inverted $^2D(9M_3 2N_1)$. When the electron proceeds in this way to infinity, we are left with a state of Cu^+ corresponding to $9M_3N_1(^3D\ ^1D)$ whereas in the normal way of ionisation, the composition of the outer shell is $10M_3$ giving $^1S_0$. The energy value of $9M_3N_1$ is less than that of $10M_3$ by $^1S_0$--$(^3D, {}^1D)$ of Cu^+, hence if the limiting value of $10M_3X_1$ (or ^2S-terms be taken O, that of $9M_3N_1$-terms will be $-\{^1S_0-(^3D,\ ^1D)\}$ of Cu^+. In other words, we have

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[1] Wentzel, Phys. Zeit., Vol. 24 (1923), p. 106.

[2] Russell and Saunders, *loc. cit.*

^2D from $9M_3N_1X_1 = {}^2S$ from $10M_3X_1 - \{^1So-(^3D, {}^1D)\}$ of Cu^+

Now, the value of the second member of the regular S-sequence is 19000, hence the second member of the inverted ^2D-group

$$=19000-\{^1S_0-(^3D, {}^1D)\} \text{ of } Cu^+$$

If $^1S_0-(^3D, {}^1D) > 19000$,

these terms will become negative.

$9M_3N_1O_1$ gives ^4D and ^2D.

The negative ^4D-terms obtained by Beals may be identified with the ^4D's of this combination. Of the other set of ^2D's, Shenstone has identified $-2349{\cdot}3$ as representing $^2D_3$ term. The only $^2D_2$ term near about is $-5664{\cdot}0$, and is probably the other component of $-2349{\cdot}3$, for the intensities of the lines which are obtained from these terms are of comparable magnitude, both giving very weak combinations.

$9M_3N_1O_1$

$^4D_1 = -2164{\cdot}3$	$^2D_2 = -5664{\cdot}0$
$^4D_2 = -1276{\cdot}5$	$^2D_3 = -2349{\cdot}3$
$^4D_3 = -640{\cdot}2$	
$^4D_4 = -95{\cdot}2$	

Sommer has also established the term $-5664{\cdot}0$ from Zeeman effect data as $^2D_2$. These ^2D terms, if this identification is correct should form the higher Rydberg sequence to the large ^2D-terms of the combination $9M_3 2N_1$. The next higher Rydberg sequence to these terms will be given by the combination, $9M_3N_1P_1$ giving ^4D and ^2D. The values of these terms will lie about 10,000 less than the values of the last given terms. A quartet D term of the right order of value and of correct intensity, and identified as such by Shenstone, has been round and is given below. There is also present a ^2D term of this value, but it is very doubtful if this can form a Rydberg sequence to the large ^2D terms, for these $^2D_{2,3} = -13138{\cdot}8,\ 147772{\cdot}3$, unlike them are not of inverted type. The observed intensities of the lines also render the identification open to doubt.

$9M_3N_1^-P_1^-$

$^4D_1 = -10641{\cdot}4$	$^2D_3 =$?
$^4D_2 = -9843{\cdot}1$	$^2D_2 =$?
$^4D_3 = -9758{\cdot}9$	
$^4D_4 = -8960{\cdot}1$	

From these the limit is calculated to lie at about $-23{,}000$, which should correspond to the difference between the deepest ^1S and ^3D of Cu$^+$.

Other sets of negative terms of values near about the same as these should be obtainable from the configuration

$9M_3''N_1N_2$ giving rise to

	^4G	$^4\overline{F}$	^4D	$^4\overline{P}$	^4S
	^2G	$^2\overline{F}$	^2D	$^2\overline{P}$	^2S
and	^2G	$^2\overline{F}$	^2D	$^2\overline{P}$	^2S

The identification of these terms is shown below.

$9M_3N_1N_2$

$^4G_3 = -10794{\cdot}6$	$^4\overline{F}_2 = -10996{\cdot}5$	$^4D_1 = -11008{\cdot}4$	$^4P_1 = -10796{\cdot}8$	
$^4G_4 = -9708{\cdot}6$	$^4\overline{F}_3 = -9843{\cdot}1$	$^4D_2 = -10890{\cdot}7$	$^4P_2 = -10425{\cdot}3$	
$^4G_5 = -8982{\cdot}4$	$^4\overline{F}_4 = -9785{\cdot}0$	$^4D_3 = -9758{\cdot}9$	$^4P_3 = -9796{\cdot}7$	
$^4G_6 = -8822{\cdot}6$	$^4\overline{F}_5 = -9670{\cdot}6$	$^4D_4 = -8960{\cdot}1$	$^4S_2 = -9619{\cdot}1$	
$^2G_4 = -8819{\cdot}7$	$^2\overline{F}_3 =$?	$^2D_2 =$?	$^2P_1 =$?	$^2S_1 =$?
$^2G_5 = -8431{\cdot}8$	$^2\overline{F}_4 = -8870{\cdot}1$	$^2D_3 =$?	$^2P_2 =$?	
$^2G_4 =$?	$^2\overline{F}_3 =$?	$^2D_2 =$?	$^2P_1 =$?	$^2S_1 =$?
$^2G_5 =$?	$^2\overline{F}_4 =$?	$^2D_3 =$?	$^2P_2 =$?	

The identification has only been partially effected. The magnetic resolution obtained by Sommer has established quite definitely the nature of the term $-9619{\cdot}1$.

II.

While the above investigation was in progress the writer had occasion to take a large number of photographs of arc and spark spectra of copper with varying degrees of excitation. It was found that an arc with high amperage—in the writer's experiments the current varied between 20 to 30 amperes—is a very fine method of obtaining lines whose intensities under different conditions are very small. The following is a list of lines which came on writer's plates, and have not been recorded by other observers. It may be mentioned here that under heavy arc conditions the impurities also appear very strongly. The lines recorded below were all observed in heavy arc.

λ	I
2276·[illegible]5	2
2300·78	1
2312·[illegible]1	3
2325·74	3
2329·[illegible]2	2
2337·12	1
2345·[illegible]0	3
2374·48	2
2383·04	1
2384·97	1
2455·20	1
2461·25	1
2461·85	1
2470·94	1
2473·49	1
2480·13	3
2482·63	1

The plates were taken on Hilger's E1 quartz spectrograph, and Hasbach's measures of copper spectrum were employed as standard lines. It may be recalled that the lines in the fourth region of the spectrograph which were measured by the writer sometime ago, were not sharp, because it was then considered necessary to tilt the prism to avoid fogging of the plate by reflected light. The present photographs have been taken by simply putting a suitable diaphragm before the prism and the resulting plates are completely free from fog and the lines also sharp and clear.

Characters of the lines.

The characters of some of the lines under varying condition were also studied. The lines 2025·3 and 2024·27 both appear in absorption in heavy arc. The former is a narrow reversal while the latter is a broad reversal 2024·27 is very sensitive to excitation and disappears completely in the spark. In the writer's opinion this settles the contention that one of them is a spark line and the other an arc line. Both of them are without doubt arc lines though they may not be related together. The case of the two very close lines 2199·56, 2199·73 which were first resolved by McLennan may also be noted. Both of them come easily reversed in heavy arc. In spark the line 2199·56 persists quite strongly, while 2199·73

The writer is greatly indebted to Prof. M. N. Saha, for interest and guidance in the present work.

On Fluctuations of Dielectric Constant in Liquids and Theories of Molecular Scattering of Light.

BY

DR. K. R. RAMANATHAN, M.A., D.SC.

I. Introduction.

In two previous papers,[1] the electromagnetic theory of the scattering of light in fluids was dealt with by the present writer from the molecular point of view. Einstein's expression for scattering was derived for liquids composed of isotropic molecules; for liquids composed of anisotropic molecules, it was shown that just as in the case of gases, there would in addition be an unpolarised scattering and expressions for the intensity and polarisation of the scattered light were derived. Gans[2] has, in the meanwhile, developed the phenomenological theory so as to include the case when the transversely scattered light is partially polarised by assuming that the fluctuations of dielectric constant which on Einstein's theory are responsible for the scattering of light, are in general anisotropic, these deviations from isotropy being also responsible for the phenomenon of electric double refraction. Some differences between the expressions for scattering put forward by Gans, by L. V. King[3] and by the present writer have shown the necessity for a re-examination of the question of fluctuations of dielectric constant in a liquid.

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[1] K. R. Ramanathan, Proc. Ind. Assoc. for Cult. of Science, Vol. VIII, Part I, pp. 1-22 and Vol. VIII, Part III, pp. 181-198 (1923). These will be referred to in the sequel as papers A and B respectively.

[2] R. Gans, Zeit. für Physik, xvii, p. 353 (1923).

[3] L. V. King; Nature, cxi, p. 667 (1923). See also paper B.

2. *Fluctuations of dielectric constant in a small volume element.*

The relation between the dielectric constant and the molecular density and polarisability which is usually used in deriving the fluctuations of dielectric constant in a liquid, is the Lorentz-Mosotti formula

$$\frac{K-1}{K+2}=\frac{4\pi}{3}nA' \qquad \ldots \quad (1)$$

where K is the dielectric constant of the liquid, n is the mean density of the molecules contained in it and A′ the average polarisability of the molecules. By differentiation,

$$dK=\frac{(K-1)\ (K+2)}{3}\left\{\frac{dn}{n}+\frac{dA'}{A'}\right\} \qquad \ldots \quad (2)$$

While there is no doubt that the above relation will be perfectly valid if the medium as a whole undergoes the change denoted by dn and dA', the validity is questionable if the particular changes are confined to a very small volume element. To see this clearly, it is necessary to recollect how the factor $(K+2)/3$ arises. The total field acting on a molecule within a liquid is obtained as follows. Consider a long cylindrical cavity described round the molecule, the axis of the cylinder being along the direction of the external field. The length of the cylinder should be very great compared with its radius and the radius, though small in the physical sense, should be many times the diameter of a molecule. The intensity at the molecule will now be Z, that of the external field. If the cavity is now filled with the molecules that have been removed, an additional intensity will be caused. The filling can be done in two steps, (1) up to the boundary of a sphere surrounding the molecule, the cylinder being tangential to the sphere and (2) within the sphere. The first of these will cause a field $\frac{4}{3}\pi nM$ at P, where M is the mean induced moment of the molecules outside the sphere. The molecules within the sphere will cause no effect at the centre provided they are arranged in cubical order with the central molecule at one of the cube corners or, on the average, when the surrounding molecules can take up continuously-varying positions and orientations as in a liquid. The resultant field will therefore be $Z+\frac{4}{3}\pi nM$ or $Z(K+2)/3$, where K is the dielectric constant of the matter outside the imaginary sphere.

If there is any local deviation of n or M in the region surrounding the molecule, it would cause an additional field whose sign may be positive or negative according to the sign of the deviation and its position with respect to the molecule. Even though the deviation is positive, it would cause a negative field if, for example, it is located in a direction at right angles to the field. When there are many such local deviations of n or M distributed at random round the molecule, the extra addition to the local field need not necessarily be proportioned to the change of nM in a small volume element round the molecule.

In obtaining the intensity of scattering from a finite volume of the liquid, we divide it into *small* volume elements and consider the waves scattered from the parts of each volume element to be coherent. The only restrictions on the size of these volume elements are that their linear dimensions should be small compared with the wave-length and that they should be sufficiently large for the fluctuations of density in one to be independent of those in another. There must be a minimum limit to the size of the volume element of a liquid under definite conditions of pressure and temperature so that the latter condition may be satisfied. This limiting volume is not easy to determine, but some idea about its magnitude can be obtained from the following considerations. Liquid benzene, for example, at 30°C. has a compressibility of 103×10^{-6} per atmosphere, which is about 1/35 of that of a perfect gas of the same molecular concentration. Since the mean square of the deviations of density in a volume element is proportional to the compressibility and since the fluctuations in a perfect gas are determined by the circumstance that the position of one molecule is uncorrelated with the positions of other molecules, we may take it that the fluctuations of density in a volume element in *liquid benzene* at 30°C. are uncorrelated with those in other volume elements if it contains on the average not less than 35 molecules. If the volume elements are so small as to contain fewer molecules than this and one of them has at a certain instant more than the average density of molecules, then other volume elements in the immediate neighbourhood will have fewer molecules, that is, the correlation between the deviations of density in neighbouring volume elements would be negative. To take another example, liquid CO_2 at 30°C. in equilibrium with its vapour has a compressibility nearly 20 times that of a perfect gas of the same molecular concentration. Here as before, the minimum size of the volume element required to justify the assumption of independence of density-fluctuations will be that it should contain not fewer than 20 molecules, but in neighbouring volume elements of smaller size than this, the fluctuations of concentration will be positively correlated. Except in the immediate neighbourhood of the critical point, we may safely take that the fluctuations of density in different volume elements are independent if they contain not less than 50 molecules.

Now, the amplitude of the scattered waves from each volume element will be proportional to the number of molecules contained in it without any regard to how they are distributed inside, and to the average field at the molecules. The value of the latter depends on the dielectric constant outside the imaginary sphere described round it. Even if we take the sphere so small that its radius is only three times the average distance between two molecules, it will contain more than 110 molecules and hence the fluctuations of density inside the sphere will have very little correlation with those outside. The volume of polarised matter responsible for the extra local field at the molecules of a volume element is thus not only larger than the volume element itself, but the fluctuations of density in are independent of those in the element. Hence, the fluctuations of local field at the molecules of a volume element will be uncorrelated with those of density in the element. Thus, in equation (1), which may also be written in the form

$$K-1=\left(\frac{K+2}{3}\right)4\pi nA',$$

the K's on the two sides of the equation are not identical; while the K on the left hand side changes with the fluctuations of density in the volume element, the K on the right hand side does not. If the latter be treated as constant,

$$dK=(K-1)\left\{\frac{dn}{n}+\frac{dA'}{A'}\right\} \qquad (3)$$

It has been tacitly assumed[1] in the above that the fluctuations of local field caused by the variations of molecular polarisability are altogether negligible. When a liquid is not subjected to electric or magnetic fields, the latter arise mainly from the varying orientations of anisotropic molecules. If we assume that the orientations of different molecules are uncorrelated with each other, the mean deviation of polarisability in a small volume element will also be uncorrelated with the average local field at the molecules since it depends mainly on the polarisation of the surrounding medium beyond the bounds of the volume element.

3. *Molecular theory of scattering.*

We may thus consider equation (3) as more correctly representing the relation between the deviations in dielectric constant, molecular concentration and molecular polarisability than equation (2). It was shown in paper A that in a medium composed of isotropic molecules, the electric intensity at a distant point P due to scattering from δv is

$$\frac{p^2}{c^2 d} \sin \theta' \, \delta v . \, Mn$$

where $p/2\pi$ is the frequency of the incident radiation, c is the velocity of light in vacuo, θ' the angle between the scattered wave and the direction of the electric vector in the incident radiation, M the moment induced in a molecule and n the density of molecules contained in the volume element. Subtracting the part common to all volume elements which would destroy each other by interference, the excess electric intensity in the scattered wave will be

$$\frac{p^2}{c^2 d} \sin \theta' (Mn - M_0 n_0) \delta v$$

where M_0 and n_0 are the mean values of the moment and density respectively.

It was assumed in paper A that M is the moment appropriate to density n, but since as we have seen, its value is not appreciably affected by the fluctuations of density, M can be equated to M_0 and the above expression will reduce to

$$\frac{p^2}{c^2 d} \sin \theta' M_0 \delta n . \delta v \qquad \ldots \quad (4)$$

and the square of the electric intensity at P due to scattering from δv will be

$$\frac{p^4}{c^4 d^2} \sin^2 \theta' \frac{(K_0 - 1)^2}{16\pi^2} Z^2 \frac{\delta n^2}{n_0^2} . \delta v^2$$

The mean value of this quantity is

$$\overline{E}^2 = \frac{p^4 \sin^2 \theta'}{c^4 d^2} \frac{(K_0 - 1)^2}{16\pi^2} Z^2 \frac{\overline{\delta n^2}}{n_0^2} \delta v^2$$

$$= \frac{\pi^2 RT\beta}{N\lambda^4} (K_0 - 1)^2 \frac{\sin^2 \theta'}{d^2} . \delta v \qquad \ldots \quad (5)$$

When the incident light is unpolarised, the intensity of the transversely scattered light from a finite volume V is

$$I=\frac{I_0V}{d^2}\,\frac{\pi^2RT\beta}{\text{[illegible]}N\lambda^4}(K_0-1)^2 \qquad \ldots \quad (6)$$

where J_0 is the intensity of the incident light. This differs from the expression given in paper A by the suppression of the factor $(K_0+2)^2/9$.[1]

Turning now to the case of a liquid composed of anisotropic molecules, the Z component of the electric intensity in the light scattered from δv at P is, as shown in page 184 of paper B

$$\frac{p^2}{c^2d}Z\left(\frac{K+2}{3}\right)L_z n\delta v \qquad \ldots \quad (7)$$

where

$$L_z=C\cos^2\theta+B\sin^2\theta\sin^2\phi+A\sin^2\theta\cos^2\phi$$

A, B and C being the polarisabilities of each molecule along three principal directions and θ, ϕ, ψ being the Eulerian angles defining the directions of the molecular axes with respect to the co-ordinate axes. The above can be written

$$\frac{p^2}{c^2d}Z\left(\frac{K+2}{3}\right)\left\{\frac{A+B+C}{3}+\left(L_z-\frac{A+B+C}{3}\right)\right\}n\delta v \qquad \ldots \quad (7a)$$

$$=\frac{p^2}{c^2d}Z\left(\frac{K+2}{3}\right)\Big\{\frac{A+B+C}{3}n_0\delta v+\frac{A+B+C}{3}\delta n\delta v$$

$$+\Big(L_z-\frac{A+B+C}{3}ndv\Big\} \qquad \ldots \quad 7(b)$$

in which $n_0+\delta n$ is substituted for n.

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[1] M. Born in his paper on Scattering in Phys. Zeit. Nr. 1/4 p. 16 (1918) and L. V. King in his letter to Nature (cxi, p. 667, 1923) have both omitted this factor, but without giving reasons.

Of the three terms in the last expression, the first is constant for every equal volume element and the third varies from molecule to molecule. When finite volume elements are considered, the first term cancels by interference, the second is summed by adding together the squares of the electric vector from the different volume elements and the third by adding together the squares of the electric vector from the different molecules. The last term is the one introduced owing to the anisotropy of the molecules. If the K in $(K+2)/3$ is taken to be the mean dielectric constant of the liquid, it can easily be shown that the total value of Z'^2 from a volume V is

$$\overline{Z'^2}=\frac{p^4}{c^4d^2}Z^2\left(\frac{K_0+2}{3}\right)^2 n_0 V\left\{\left(\frac{A+B+C}{3}\right)^2\frac{RT\beta n_0}{N}+\frac{4}{3}f\right\}$$

where

$$f=\tfrac{1}{15}(A^2+B^2+C^2-AB-BC-CA)$$

As was shown in paper B (equation 1)

$$\overline{X'^2}=\frac{p^4}{c^4d^2}Z^2\left(\frac{K_0+2}{3}\right)^2 f n_0 V$$

Hence

$$\frac{\overline{X'^2}}{\overline{Z'^2}}=\frac{f}{\left(\frac{A+B+C}{3}\right)^2\frac{RT\beta n_0}{N}+\frac{4}{3}f}$$

If the incident light is unpolarised, the ratio of the weak component to the strong in the transversely scattered light is

$$r=\frac{2f}{\left(\frac{A+B+C}{3}\right)^2\frac{RT\beta n_0}{N}+\frac{4}{3}}$$

$$=\frac{6\delta}{\frac{5RT\beta n_0}{N}+7\delta} \qquad \ldots \quad (8)$$

where

$$\delta=(A^2+B^2+C^2-AB-BC-CA)/(A+B+C^2)$$

And the intensity of the light scattered in the transverse direction expressed in terms of r is

$$\frac{I_0 V}{d^2} \frac{RT\beta}{2N\lambda^4}(K_0-1)^2 \frac{6(1+r)}{6-7r} \qquad (9)$$

The value of the co-efficient of attenuation can easily be shown to be

$$h = \frac{8\pi^3}{3} \frac{RT\beta}{N\lambda^4}(K_0-1)^2 + \frac{8\pi^3}{3n_0\lambda^4}(K_0-1)^2\, 2\delta$$

$$= \frac{8\pi^3}{3n_0\lambda^4}(K_0-1)^2 \left\{\frac{RT\beta n_0}{N} + 2\delta\right\} \quad \ldots \quad (10)$$

4. *Gans's theory of scattering.*

Lord Rayleigh's expression for the scattering of light by a particle whose linear dimensions are small in comparison with the wave-length, when its dielectric constant differs by only a small amount from that of the surrounding medium, takes the form[1]

$$\frac{I}{I_0} = \frac{\pi^2 \Lambda^2}{2\lambda^4 d^2} (\delta v)^2 \, (1+\cos^2\chi) \quad \ldots \quad (11)$$

where Λ is the deviation in dielectric constant of the particle, χ is the angle between the incident and scattered beams, and δv is the volume of the particle. When we substitute for Λ^2 the mean value of the square of the fluctuations of dielectric constant taking place in a volume element δv of a pure liquid and assume that these are solely caused by the fluctuations of density, we have

$$\overline{\Lambda^2} = \left(\frac{\delta K}{\delta\rho}\right)^2 \overline{\delta\rho^2}$$

$$= \left(\frac{\delta K}{\delta\rho}\right)^2 \frac{RT\beta}{N\delta v} \rho^2$$

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[1] Lord Rayleigh, Scientific papers, Vol. i, p. 526.

and equation (11) becomes

$$\rho^2 \left(\frac{\delta K}{\delta \rho}\right)^2 \delta v \, (1 + \cos^2 \chi) \qquad \ldots \quad (12)$$

which can easily be seen to be identical with Einstein's expression.

If now we consider the deviations of dielectric constant of a volume element δv to be anisotropic, the intensity of scattering will be increased and the transversely scattered light will also appear partially polarised. Let Λ_1, Λ_2, Λ_3 be the deviations of optical dielectric constant of a volume element δv along three principal directions of anisotropy and let $\Lambda_1 = \Lambda + \lambda_1$, $\Lambda_2 = \Lambda + \lambda_2$, $\Lambda_3 = \Lambda + \lambda_3$, $\overline{\lambda_1} + \overline{\lambda_2} + \overline{\lambda_3}$ being equal to zero. Then Λ is the purely isotropic part of the deviations and λ_1, λ_2, λ_3 the purely anisotropic part. $\overline{\Lambda^2}$ is identified with the $(\delta K/\delta \rho)^2 \, \delta \rho^2$ of Einstein's theory. Gans showed that the imperfection of polarisation of the scattered light in a direction at right angles to the incident unpolarised beam, which is measured by the ratio of the intensity of the weak component that of the strong is given by

$$r = \frac{(\overline{\Lambda_1^2} + \overline{\Lambda_2^2} + \overline{\Lambda_3^2}) - 2\,(\overline{\Lambda_1 \Lambda_2} + \overline{\Lambda_2 \Lambda_3} + \overline{\Lambda_3 \Lambda_1})}{4(\overline{\Lambda_1^2} + \overline{\Lambda_2^2} + \overline{\Lambda_3^2}) + (\overline{\Lambda_1 \Lambda_2} + \overline{\Lambda_2 \Lambda_3} + \overline{\Lambda_3 \Lambda_1})} \qquad (13)$$

and the intensity in the same direction from a volume δv by

$$\frac{I}{I_0} = \frac{\pi^2 \overline{\Lambda^2}}{2 \lambda^4 d^2} (\delta v)^2 \, \frac{6 + 6r}{6 - 7r} \qquad \ldots \quad (14)$$

This differs from the expression on the right-hand side of (11) (with $\chi = \pi/2$) by the introduction of the factor

$6(1+r)/(6-7r)$. The co-efficient of attenuation was obtained by Gans to be

$$h = \frac{8\pi^2}{3\lambda^4} \frac{\overline{\Lambda_1^2} + \overline{\Lambda_2^2} + \overline{\Lambda_3^2}}{3} \delta v$$

$$= \frac{8\pi^2}{3\lambda^4}\left(\overline{\Lambda^2} + \frac{\overline{\lambda_1^2} + \overline{\lambda_2^2} + \lambda_3^2}{3} \right) \delta v \qquad \dots \quad (15)$$

Gans next connects the anisotropic part of the fluctuations of dielectric constant with the Kerr constant of electric double refraction somewhat on the same lines as in Langevin's work connecting molecular anisotropy with electric double refraction. It may be useful to give a summary of Gans's treatment. If anisotropic fluctuations of dielectric constant occur in a liquid, there will also be similar fluctuations of electrostatic dielectric constant. In an isotropic liquid, the fluctuations will be in random directions, but when an electrostatic field is put on, the directions will no longer be random, but there will be a tendency for the largest of the three principal dielectric constants to set themselves along the direction of the field, so that when a beam of light is passed through the medium perpendicular to the field, the velocities of the components parallel and perpendicular to it will be unequal, that is, the medium will become doubly refracting. If Λ_1°, Λ_2°, Λ_3° be the three principal deviations of electrostatic dielectric constant of a volume element and they make angles whose cosines are γ_1, γ_2 and γ_3 with the applied electrostatic field E_0 (parallel to OZ), then the difference of potential energy of the volume element from that of an isotropic volume element containing the same mass but having the mean dielectric constant of the liquid is

$$-\frac{E_0^2}{8\pi} \delta v(\Lambda_1^\circ\gamma_1^2 + \Lambda_2^\circ\gamma_2^2 + \Lambda_3^\circ\gamma_3^2) \qquad \dots \quad (16)$$

By Boltzmann's theorem, the probability that one of the principal axes of a volume element has its direction between

θ and $\theta+d\theta$, ϕ and $\phi+d\phi$, and ψ and $\psi+d\psi$, where θ is the angle between the direction of the field and the axis under consideration and ϕ and ψ have their usual significance, is

$$e^{Q(\Lambda_1^0\gamma_1^2+\Lambda_2^0\gamma_2^2+\Lambda_3^0\gamma_3^2)}\sin\theta\, d\theta\, d\phi\, d\psi$$

where

$$Q=E_0^2 N\,\delta v/8\pi RT$$

By the usual method of obtaining mean values

$$\overline{\gamma_1^2}=\frac{\iiint \gamma_1^2 e^{Q(\Lambda_1^0\gamma_1^2+\Lambda_2^0\gamma_2^2+\Lambda_3\gamma_3^2)}\sin\theta\, d\theta\, d\phi\, d\psi}{\iiint e^{Q(\Lambda_1^0\gamma_1^2+\Lambda_2^0\gamma_2^2+\Lambda_3^0\gamma_3^2)}\sin\theta\, d\theta\, d\phi\, d\psi}$$

Reducing, we get

$$\overline{\gamma_1^2}=\frac{1}{3}+\frac{2Q}{15}\left(\Lambda_1^0-\frac{\Lambda_1^0+\Lambda_2^0+\Lambda_3^0}{3}\right)$$

$$\overline{\gamma_2^2}=\frac{1}{3}+\frac{2Q}{15}\left(\Lambda_2^0-\frac{\Lambda_1^0+\Lambda_2^0+\Lambda_3^0}{3}\right)$$

and

$$\overline{\gamma_3^2}=\frac{1}{3}+\frac{2Q}{15}\left(\Lambda_3^0-\frac{\Lambda_1^0+\Lambda_2^0+\Lambda_3^0}{3}\right) \qquad \ldots (17)$$

Gans takes the change of dielectric constant of the medium as a whole in the direction of the Z-axis to be the average change of dielectric constant of the volume elements composing it, in that direction. Thus

$$K_z-K_0=\overline{(\Lambda_1\overline{\gamma_1^2}+\Lambda_2\overline{\gamma_2^2}+\Lambda_3\overline{\gamma_3^2})} \qquad \ldots (18)$$

Substituting the value for $\overline{\gamma_1^2}$, $\overline{\gamma_2^2}$, $\overline{\gamma_3^2}$ and remembering that

$\overline{\Lambda_1}+\overline{\Lambda_2}+\overline{\Lambda_3}=0$,

$$K_z-K_0=\frac{2Q}{15}\left\{\overline{(\Lambda_1^0\Lambda_1}+\overline{\Lambda_2^0\Lambda_2}+\overline{\Lambda_3^0\Lambda_3)}-\frac{\overline{(\Lambda_1^0+\Lambda_2^0+\Lambda_3^0)}\;\overline{(\Lambda_1+\Lambda_2+\Lambda_3)}}{3}\right\} \qquad (19)$$

Similarly, evaluating $\overline{a_1^2}$, $\overline{a_2^2}$ $\overline{a_3^2}$ where a_1, a_2, a_3 are the angles made by the directions of Λ_1^0, Λ_2^0, Λ_3^0 with OX he gets

$$\overline{a_1^2}=\frac{1}{3}-\frac{Q}{15}\left(\Lambda_1^{\circ}-\frac{\Lambda_1^{\circ}+\Lambda_2^{\circ}+\Lambda_3^{\circ}}{3}\right)$$

with similar expressions for $\overline{a_2^2}$ and $\overline{a_3^2}$.

$$K_z-K_0=\overline{\Lambda_1\overline{a_1^{2}}+\Lambda_2\overline{a_2^{2}}+\Lambda_3\overline{a_3^{2}}}$$

$$=-\frac{Q}{15}\left(\overline{\Lambda_1^{\circ}\Lambda_1}+\overline{\Lambda_2^{\circ}\Lambda_2}+\overline{\Lambda_3^{\circ}\Lambda_3}\right.$$

$$\left.-\frac{\overline{(\Lambda_1^{\circ}+\Lambda_2^{\circ}+\Lambda_3^{\circ})}\,\overline{(\Lambda_1+\Lambda_2+\Lambda_3)}}{3}\right) \quad \ldots \quad (20)$$

If we write ν_z and ν_x for the refractive indices for vibrations parallel and perpendicular to the field (ν_z^2 being equal to K_z) etc., and ν for the mean refractive index,

$$\frac{\nu_z-\nu_x}{E_0^2}=\frac{N\delta v}{80\pi\nu RT}\left\{\overline{\Lambda_1^{\circ}\Lambda_1}+\overline{\Lambda_2^{\circ}\Lambda_2}+\overline{\Lambda_3^{\circ}\Lambda_3}\right.$$

$$\left.-\frac{\overline{(\Lambda_1^{\circ}+\Lambda_2^{\circ}+\Lambda_3^{\circ})}\,\overline{(\Lambda_1+\Lambda_2+\Lambda_3)}}{3}\right\} \quad \ldots \quad (21)$$

Assuming that

$$\frac{\Lambda_1^{\circ}}{\Lambda_1}=\frac{\Lambda_2^{\circ}}{\Lambda_2}=\frac{\Lambda_3^{\circ}}{\Lambda_3}=\frac{(\epsilon-1)(\epsilon+2)}{(\nu^2-1)(\nu^2+2)} \quad \ldots \quad (22)$$

where ϵ is the electrostatic dielectric constant, equation (21) becomes

$$\frac{\nu_z-\nu_x}{E_0^2}=\frac{N\delta v}{80\pi\nu RT}\,\frac{(\epsilon-1)(\epsilon+2)}{(\nu^2-1)(\nu^2+2)}\left\{\overline{\Lambda_1^2}+\overline{\Lambda_2^2}+\overline{\Lambda_3^2}-\frac{\overline{(\Lambda_1+\Lambda_2+\Lambda_3)^2}}{3}\right\}$$

$$=\frac{N\delta v}{80\pi\nu RT}\,\frac{(\epsilon-1)(\epsilon+2)}{(\nu^2-1)(\nu^2+2)}\left(\overline{(\lambda_1^2}+\overline{\lambda_2^2}+\overline{\lambda_3^2}\right)$$

Since the Kerr constant

$$B' = (\nu_s - \nu_e)/\lambda E_0^2$$

$$\overline{\lambda_1^2} + \overline{\lambda_2^2} + \overline{\lambda_3^2} = \frac{80\pi\nu RT\lambda B'(\nu^2-1)(\nu^2+2)}{N\delta v(\epsilon-1)(\epsilon+2)} \quad \ldots \quad (23)$$

Substituting this value in (15) and writing

$$\overline{\Lambda^2} = \frac{(\nu^2-1)^2(\nu^2+2)^2}{9} \quad \frac{RT\beta}{N\delta v}$$

Gans obtains the co-efficient of attenuation to be

$$h = \frac{8\pi^3}{3}\,\frac{RT}{N\lambda^4}\left\{\frac{\beta(\nu^2-1)^2(\nu^2+2)^2}{9} + \frac{80\pi\nu\lambda B'}{3}\,\frac{(\nu^2-1)(\nu^2+2)}{(\epsilon-1)(\epsilon+2)}\right\} \ldots \quad (24)$$

5. *Discussion of Gans's theory.*

The quantity

$$\overline{\lambda_1^2} + \overline{\lambda_2^2} + \overline{\lambda_3^2}$$

which is determined in (23) differs, however, in an important way from the same expression in (15). Gans's assumption in (22) that

$$\Lambda_1^0/\Lambda_1 \text{ etc.} = \frac{(\epsilon-1)(\epsilon+2)}{(\nu^2-1)(\nu^2+2)}$$

is equivalent to assuming

$$\lambda_1^0/\lambda_1, \text{ etc.} = (\epsilon-1)(\epsilon+2)/(\nu^2-1)(\nu^2+2),$$

as can easily be seen by reducing (21) in terms of Λ^0, Λ and λ_1^0, λ_1, etc. In a liquid under ordinary conditions, the anisotropic fluctuations of dielectric constant of different volume elements (even when they are very small and contain only a few molecules) are entirely uncorrelated with each other, but when the liquid is placed in an electrostatic field, the axis of largest dielectric constant in each volume element tends to place itself parallel to the field. The resulting change in dielectric constant is conditioned not only by the turning of the anisotropic volume elements, but also by the change in local field produced by such *general* turning. The potential energy of an anisotropic volume element when the medium is placed in an electrostatic field E_0 is written by Gans to be

$$\frac{-E_0^2}{8\pi}(\Lambda_1^0\gamma_1^2+\Lambda_2^0\gamma_2^2+\Lambda_3^0\gamma_3^2)\delta v, \qquad \dots \quad (25)$$

This may also be written

$$\frac{-E_0^2\delta v}{8\pi}\left\{\Lambda^0+(\lambda_1^0\gamma_1^2+\lambda_2^0\gamma_2^2+\lambda_3^0\gamma_3^2)\right\} \qquad \dots \quad (26)$$

Now, $\lambda_1^0\gamma_1^2+\lambda_2^0\gamma_2^2+\lambda_3^0\gamma_3^2$ is the anisotropic deviation in dielectric constant in the direction of the field if the change due to the field is confined to the particular volume element so that the local polarisation field is not affected. But since a correlated change of dielectric constant is suffered by every volume element, the actual anisotropic deviation in dielectric constant will be

$$\left(\frac{\epsilon+2}{3}\right)(\lambda_1^0\gamma_1^2+\lambda_2^0\gamma_2 +\lambda_3^0\gamma_3^2)$$

[compare equations (2) and (3)] and the second term in expression (26) for the potential energy will become

$$-\frac{E_0^2\delta v}{8\pi}\left\{\frac{\epsilon+2}{3}\right\}(\lambda_1^0\gamma_1^2+\lambda_2^0\gamma_2^2+\lambda_3^0\gamma_3^2) \qquad \dots \quad (27)$$

This term alone is of importance in determining electric double refraction. $\overline{\gamma_1^2}$ will therefore become equal to

$$\frac{1}{3}+\frac{2Q}{15}\left(\frac{\epsilon+2}{3}\right)\left(\lambda_1^0-\frac{\lambda_1^0+\lambda_2^0+\lambda_3^0}{3}\right)$$

and $\overline{\gamma_2^2}$ and $\overline{\gamma_3^2}$ will also get similarly altered.

Expression (18) will also get changed to

$$K_s - K_0 = \left(\frac{\nu^2+2}{3}\right)\left(\overline{\lambda_1\overline{\gamma_1^{\,2}} + \lambda_2\overline{\gamma_2^{\,2}}} \; \overline{+\lambda_3\overline{\gamma_3^{\,2}}}\right)$$

$\overline{\Lambda_1} + \overline{\Lambda_2} + \overline{\Lambda_3}$ being equal to zero.

Therefore,

$$\frac{K_s - K_x}{E_0^{\,2}} = \frac{N\delta v}{40\pi RT}\left(\frac{\epsilon+2}{3}\right)\left(\frac{\nu^2+2}{3}\right)\frac{\lambda_1^{\,0}}{\lambda_1}\cdot\left\{\overline{\lambda_1^{\,2}} + \overline{\lambda_2^{\,2}} + \overline{\lambda_3^{\,2}} - \frac{\overline{(\lambda_1+\lambda_2+\lambda_3)^2}}{3}\right\} \quad \ldots \quad (28)$$

If the average field acting on the molecules of a small volume element in the absence of an electrostatic field is unaffected by the anisotropic fluctuations of dielectric constant and if we assume that the directions of the principal electrostatic and optical polarisabilities in each molecule are the same and their magnitudes are proportional to each other,

$$\frac{\lambda_1^{\,0}}{\lambda_1} = \frac{\epsilon-1}{\nu^2-1}$$

and

$$\frac{\nu_s - \nu_x}{E_0^{\,2}} = \frac{N\delta v}{80\pi\nu RT}\;\frac{\epsilon-1}{\nu^2-1}\cdot\frac{\epsilon+2}{3}\cdot\frac{\nu^2+2}{3}\cdot\left(\overline{\lambda_1^{\,2}} + \overline{\lambda_2^{\,2}} + \overline{\lambda_3^{\,2}}\right)$$

$$= \frac{N\delta v}{80\pi\nu RT}\;\frac{(\epsilon-1)(\epsilon+2)}{(\nu^2-1)(\nu^2+2)}\left(\frac{\nu^2+2}{3}\right)^2\cdot\left(\overline{\lambda_1^{\,2}} + \overline{\lambda_2^{\,2}} + \overline{\lambda_3^{\,2}}\right)$$

$$\therefore\; \left(\overline{\lambda_1^{\,2}} + \overline{\lambda_2^{\,2}} + \overline{\lambda_3^{\,2}}\right) = \frac{80\pi\nu RT \quad \lambda B^1. \quad (\nu^2-1)(\nu^2+2)}{N\delta v \quad (\epsilon-1)\;(\epsilon+2)}\cdot\frac{9}{(\nu^2+2)^2} \qquad (29)$$

If at the same time for reasons discussed in section I, we take

$$\overline{\Lambda_1^{*2}} \overset{*}{=} \frac{(\nu^2-1)^2 RT\beta}{N\delta v},$$

Gans's expression (24) for h will get transformed into

$$h=\frac{8\pi^3}{3}\ \frac{RT}{N\lambda^4}l.\left\{\beta(\nu^2-1)^2\ \frac{80\pi\nu\lambda B^1}{(\nu^2+2)}\cdot\frac{(\nu^2-1).\,3}{(\epsilon-1)(\epsilon+2)}\right\}\quad\ldots\quad(30)$$

6. *Anisotropic fluctuations of dielectric constant in terms of molecular constants.*

It can easily be seen that anisotropic fluctuations of dielectric constants of small volume elements are a necessary consequence of the anisotropy of the individual molecules. Consider a small volume element of an isotropic liquid composed of anisotropic molecules. Since the molecular axes are by hypothesis oriented at random, the number of molecules pointing in directions included within any small solid angle will not, in general, be exactly the same as the number pointing in directions included within another equal solid angle pointing in some other direction. Thence will arise a residual anisotropy of the volume element whose magnitude and direction will vary from instant to instant. The smaller the number of molecules, the greater will be the fluctuations from isotropy.

We have already seen that in a small volume element of of an isotropic liquid under normal conditions

$$\delta K=(K_0-1)\left(\frac{\delta n}{n}+\frac{\delta A'}{A'}\right)$$

$$\therefore\quad \overline{\delta K^2}=(K_0-1)^2\left\{\frac{\overline{\delta n^2}}{n^2}+\frac{\overline{\delta A'^2}}{A'^2}\right\}\quad\ldots\quad(31)$$

where it is assumed that δn and $\delta A'$ are independent of each other. The first term of the above equation can be identified with $\overline{\Lambda^2}$ and the second with

$$(\overline{\lambda_1^2}+\overline{\lambda_2^2}+\overline{\lambda_3^2})/3.$$

It suffices now to evaluate

$$\overline{\delta A'^2}/A'^2.$$

When a unit field parallel to the axis of Z is applied to the medium, the mean value of the square of the sum of the induced moments of the molecules is [See 7(a) and 7(b) above]

$$\overline{\left\{\frac{A+B+C}{3}\right\}^2 n^2\delta v^2} + \Sigma\left\{L_3 - \frac{A+B+C}{3}\right\}^2$$

$$=\left(\frac{A+B+C}{3}\right)^2 n_0^2\delta v^2 + \overline{\left(\frac{A+B+C}{3}\right)^2 \delta n^2\delta v^2} + n_0\delta v.\tfrac{4}{3}f$$

Of these, only the last term contributes to $\delta A'^2$. The mean value of the squares of the moments induced parallel to the X and Y axis will each be

$$n_0\delta v.\,f. \qquad \text{(Paper B, Eq, 1)}$$

$$\therefore \quad \overline{\delta A'^2} = \frac{n_0\delta v.(\frac{4}{3}f+2f)}{n_0^2\delta v^2} = \frac{10}{3}f\Big/n_0\delta v. \qquad \ldots \quad (32)$$

and

$$\frac{\overline{\lambda_1^2}+\overline{\lambda_2^2}+\overline{\lambda_3^2}}{3} = (K_0-1)^2\,\frac{\frac{10}{3}\cdot\frac{1}{15}(A^2+B^2+C^2-AB-BC-CA)}{\left(\frac{A+B+C}{3}\right)^2 n_0\delta v}$$

$$=\frac{2(K_0-1)^2(A^2+B^2+C^2-AB-BC-CA)}{(A+B+C)^2 n_0\delta v}$$

$$=\frac{2(K_0-1)^2\delta}{n_0\delta v} = \frac{2(\mu^2-1)^2\delta}{n_0\delta v} \qquad \ldots \quad (33)$$

Identifying this $\overline{\lambda_1^2}+\overline{\lambda_2^2}+\overline{\lambda_3^2}$ derived from *a priori* considerations with the same quantity expressed in terms of the Kerr constant in (29), we can express B^1 in terms of δ

$$B'=\frac{(\nu^2-1)(\nu^2+2)(\epsilon-1)(\epsilon+2)N\delta}{120\pi RTn_0\nu\lambda} \tag{34}$$

on the assumption that the principal axes of dielectric and optical constants are parallel and proportional to each other. This is the same expression as is obtained on Langevin's theory of electrical double refraction.[1]

In terms of molecular constants,

$$h=\frac{8\pi}{3\lambda^4}\left\{\overline{\Lambda^2}+\frac{\overline{\lambda_1^2}+\overline{\lambda_2^2}+\overline{\lambda_3^2}}{3}\right\}\delta v$$

$$=\frac{8\pi}{3n_0\lambda^4}\left\{\frac{RT\beta n_0}{N}+2\delta\right\}(K_0-1)^2 \qquad \ldots \quad (35)$$

which is identical with (10).

The expression for the intensity in a transverse direction also becomes the same as (9).

7. *Comparison of phenomenological and molecular theories.*

We see from the above that both the phenomenological and molecular theories lead exactly to the same result, and this is what is to be expected. Strictly, the phenomenological theory itself is partly molecular, since in developing it, we have to use the Lorentz formula of refraction which is based on molecular considerations. As regards the theory of electric double refraction, the advantage lies with the molecular way of treatment. It is more direct and simple and is capable of extension to the case when the molecules possess a permanent electric moment.[1] And since we know for a certainty from the partial polarisation of the transversely scattered light in gases and vapours that molecules are in general optically anisotropic, there is nothing to be gained by avoiding that assumption and preferring instead the assumption of anisotropic dielectric constants of small elements of volume.

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[1] P. Debye, Handbuch der Radiologie, Band VI, p. 768. Also K. S. Krishnan, Proc. Ind. Assoc. Cult. of Science, Vol. IX, Part IV, p. 251.

In a recent paper, Mr. K. S. Krishnan[2] has compared the available experimental data on light-scattering in liquids with different formulæ that have been proposed from time to time and shown that so far as comparative values of intensities are concerned, relation (9) is in better agreement with experiment than the formulæ involving $(K+2)^2/9$ as a factor. As regards absolute measurements, the data are not decisive, but it is hoped that results of critical measurements of intensity in a few selected liquids will soon be available to decide the question. Measurements near the critical temperature are not of much help in this respect, as the values of $(K+2)^2/9$ in that region generally differ very little from unity.

Mr. Krishnan has utilized the data about polarisation to calculate the values of δ which gives a measure of the optical anisotropy of the molecule and compared them with the values calculated from the Kerr constant of electric double refraction according to (34). Here again, he finds that values of δ given by the revised expressions are in better agreement with the values calculated from the Kerr constant. It may be mentioned that liquids containing polar molecules are excluded from consideration.

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[1] C. V. Raman and K. S. Krishnan, Nature, Vol. 118, p. ; also same authors Phil. Mag., Vol. 3, pp. 713-723 and pp. 724-735, April 1927.

[2] K. S. Krishnan, *loc. cit.*

8. *Binary Liquid Mixtures.*

The arguments discussed in Sections 1 and 2 should also be applicable to the fluctuations of concentration in a binary liquid mixture. In a detailed paper[1] on the "Opalescence of binary liquid mixtures," Dr. J. C. K. Rav has obtained the following expression for the intensity of the transversely scattered light from a volume V

$$\frac{p^4Z^2}{c^4d^2}V\left\{\frac{13}{3}\cdot\left(\frac{K+2}{3}\right)^2(f_1n_1+f_2n_2)+\frac{(K-1)^2(K+2)^2}{144\pi^2}\cdot\frac{RT\beta}{N}\right.$$

$$\left.+\frac{1}{16\pi^2}\cdot\frac{M_2}{Nm_1}\,\frac{(\partial K/\partial k)^2}{\partial\log p_2/\partial k}\right\} \quad \ldots \quad (36)$$

(See equation 41 on p. 45) where f_1, f_2 are the values of f which is equal to

$$\tfrac{1}{15}(A^2+B^2+C^2-AB-BC-CA)$$

for the first and second components respectively, n_1, n_2 are the numbers of molecules of the two components per unit of volume, M_2 is the molecular weight in the gaseous phase and p_2 the partial vapour pressure, of the second component, m_1 and m_2 are the masses of the first and second components in unit volume of the mixture and k is the fraction m_2/m_1. The factor $(K+2)^2/9$ in the second term is introduced in the same manner as in the previous treatments of liquids with isotropic molecules, that is, assuming that the local field in a small volume element changes with the changes of density in the element. According to section 2, this factor should be omitted.

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[1] J. C. K. Rav. Proc. Ind. Assoc. for Cult. of Science, Vol. IX, Part I, p. 19 (1924).

$\partial K/\partial k$ in the third term is obtained by measuring the tangent at desired points from a graph showing the variation of K with k. These values are appropriate to the case where similar changes of concentration occur throughout the liquid. When the deviations of concentration from normal in different volume elements are uncorrelated with each other, the changes of dielectric constant in them will be due solely to these changes of concentration and the local field will remain unaffected. The values of $\partial K/\partial k$ which we should adopt are therefore not those obtaining when similar changes of concentration occur throughout the liquid, but these values divided by a factor $(K+2)/3$. Making these changes, expression (36) will become

$$\frac{p^4 Z^2}{c^4 d^2} V \left\{ \frac{13}{3}\frac{(K+2)^2}{9}(f_1 n_1 + f_2 n_2) + \frac{(K-1)^2}{16\pi^2}\frac{RT\beta}{N} \right.$$

$$\left. + \frac{1}{16\pi^2}\frac{M_2(\partial K/\partial k)^2}{N m_1 \partial \log p_2/\partial k}\cdot\frac{9}{(K+2)^2} \right\} \qquad \ldots \quad (37)$$

and equation (40) of Dr. Rav's paper for the depolarisation of the transversely scattered light will be changed to

$$\frac{\dfrac{2(K+2)^2}{9}(f_1 n_1 + f_2 n_2)}{\dfrac{7}{3}\left(\dfrac{K+2}{3}\right)^2(f_1 n_1 + f_2 n_2) + \dfrac{(K-1)^2}{16\pi^2}\dfrac{RT\beta}{N} + \dfrac{9}{16\pi^2(K+2)^2}\,\dfrac{M_2(\partial K/\partial k)^2}{N m_1 \partial \log p_2/\partial k}}$$

The available experimental data are not sufficiently accurate to decide whether these or Dr. Rav's expressions better represent the facts.

9. *Summary.*

In this paper, the question of fluctuations of dielectric constant of a small volume element of a liquid is discussed with reference to the theories of molecular scattering of light. Reasons are given for concluding that the fluctuations of dielectric constant responsible for scattering cannot be determined by differentiating Lorentz's relation between dielectric constant and density but that the factor $(K+2)/3$ must be omitted from the expression for δK. Revised expressions for the intensity and polarisation of the scattered light are given in terms of the molecular theory.

Gans's phenomenological method of treatment is outlined and discussed and the assumptions underlying it pointed out. If the omission of the $(K+2)/3$ factor of the expression for δK be accepted, Gans's theory and molecular theory lead to identical results.

It is shewn that if the molecules of a liquid are anisotropic, small volume elements must necessarily possess accidental deviations from isotropy; the relation between them, the constants of molecular anisotropy and the Kerr constant of electric double refraction is worked out.

Mr. Krishnan has shown that results of experiments are favourable to the omission of the factor $(\nu^2+2)^2/9$.

It is pointed out that similar arguments should hold in the case of binary liquid mixtures and that the fluctuations of concentration accidentally occurring in such a mixture cannot be assumed to be identical with the changes of

dielectric constant with concentration obtained from experiments on liquids in mass. Revised expressions for scattering are given.

I wish to express my thanks to Prof. C. V. Raman for his kind interest in the work.

The Energy of the Struck String

By Panchanon Das, M.Sc.

In a recent paper,[1] Messrs. W. H. George and H. E. Beckett, have broken new ground in the experimental study of the motion of pianoforte strings. Instead of applying the usual method[2] of analysing the overtones, they have measured the energy communicated to the string by the impinging hammer supposed to be rigid, and have supplied very valuable experimental data by way of tables and graphs, which can be made use of in testing the various theories advanced so far. They have already tested the original Kaufmann theory and found that the agreement is good so long as the striking-length is not very large. (Figs. 10—16 in the paper cited.) In the present paper an attempt will be made to interpret their experimental results with the help of Kaufmann's formula as extended by Das.[3] It has been found that Das's formula gives a much better, though not complete, explanation of the dynamical behaviour of the string, even when the striking-length is so large that *reflections from both ends* affect the motion of the hammer, specially if the hammer is very light. Here it will be useful to give at first a brief resumé of the formulae obtained by Das. The following are the symbols used in this paper:—

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[1] Proc. Roy. Soc. Vol. 114, p. 111, Feb. 1927.

[2] S. K. Datta, Proc. Ind. Assn. Cultn. Sc., Vol. VIII, p. 107, 1923.

[3] P. Das, Proceedings of the Indian Association for the Cultivation of Science., Vol. VII, p. 13, 1921; Vol. IX, p. 297, 1926; and Vol. X., p. 75, 1926. These papers will be referred to as papers No. A, B and C respectively.

m = Mass of hammer.
ρ = Mass per unit length of string.
c = Wave-velocity along string.
V = Initial velocity of hammer.
v = Final velocity of hammer.
$a = -2\rho/\mathrm{m}$.
F = Pressure of hammer.
a = Striking-length of string.
l = Total length of string.
$b = 1 - \mathrm{a}$.

A and B are the fixed points between which the string is stretched and O is the point on it, where the hammer strikes it. Let OA=a, and OB=b. Then the intervals of time taken by the pulse generated by the impact in reaching the hammer again after reflection from the ends A and B are 2a/c and 2b/c respectively. These reflected pulses on reaching the hammer give rise to secondary pulses which again come back to the hammer after reflection from the ends in the same respective intervals of time.

This process goes on until the hammer leaves the string. Thus the motion *during the impact* is sharply divided into two sets of Epochs of magnitudes $2a/c$ and $2b/c$ respectively and the nature of motion is different in different Epochs.

If the length b is so much larger than the length a, that the impact terminates before the reflection from the end B reaches the hammer, then the motion is characterised by one set of Epochs, *viz.*, those relative to the end A only. Under such circumstances the pressure F of the hammer can be expressed[1] as follows :—

I Epoch ($0 < ct < 2a$):—

$$\mathrm{F}_1(ct) = 2\rho \mathrm{V} c e^{act} \qquad \ldots \quad (1)$$

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[1] Paper No. A, p. 19.

II Epoch ($2a < ct < 4a$) :—

$$F_2(ct)=2\rho Vc\left[e^{act}+e^{\alpha(ct-2a)}\left\{1+a(ct-2a)\right\}\right] \quad \dots \quad (2)$$

III Epoch ($4a < ct < 6a$)

$$F_3(ct)=2\rho Vc\left[e^{act}+e^{\alpha(ct-2a)}\left\{1+\alpha(ct-2a)\right\}\right.$$

$$\left.+e^{\alpha(ct-4a)}\left\{1+2a(ct-4a)+\frac{a^2}{\lfloor\underline{2}}(ct-4a)^2\right\}\right] \quad \dots \quad (3)$$

IV Epoch ($6a < ct < 8a$) :—

$$F_4(ct)=2\rho Vc\left[e^{act}+e^{\alpha(ct-2a)}\left\{1+\alpha(ct-2a)\right\}\right.$$

$$+e^{\alpha(ct-4a)}\left\{1+2a(ct-4a)+\frac{a^2}{\lfloor\underline{2}}(ct-4a)^2\right\}$$

$$+e^{\alpha(ct-6a)}\left\{1+3a(ct-6a)+\frac{3a^2}{\lfloor\underline{2}}(ct-6a)^2\right.$$

$$\left.\left.\frac{a^3}{\lfloor\underline{3}}(ct-6a)^3\right\}\right] \quad \dots \quad (4)$$

And so on.

It appears logical to assume that the hammer leaves the string, when the pressure $F=0$. Thus the duration of contact between the hammer and the string is the smallest root of $F=0$. We thus see that the impact cannot terminate within the I Epoch, since the root is infinite. If the impact extends to the II Epoch, the duration of the same is given by[1]

$$act=2a-\frac{1}{a}\left(1+e^{2aa}\right) \quad \dots \quad (5)$$

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[1] Paper No. C, p. 95.

If the impact extends to the III Epoch, the duration is given by[1]

$$\alpha ct = 4a\alpha - \left(2 + e^{2a\alpha}\right) + \sqrt{2 + 2(1 + 2a\alpha)e^{2a\alpha} - e^{4a\alpha}} \quad \ldots \quad (6)$$

If it extends to IV Epoch, the duration may be approximately found[2] in the form :—

$$\alpha ct = 7a\alpha - \frac{1}{\alpha} \cdot \frac{F_4(7a)}{F_4'(7a)} \quad \ldots \quad (7)$$

And so on.

It has also been shown,[3] that the velocities v of the hammer during the II, III and IV Epochs, are respectively given by

$$\text{(II Epoch), } \frac{v}{V} = e^{\alpha ct} + \alpha(ct - 2a)\, e^{\alpha(ct-2a)} \quad \ldots \quad (8)$$

$$\text{(III Epoch), } \frac{v}{V} = e^{\alpha ct} + \alpha(ct - 2a)e^{\alpha(ct-2a)}$$

$$+ e^{\alpha(ct-4a)} \left\{ \alpha(ct - 4a) + \frac{\alpha^2}{\lfloor 2}(ct - 4a)^2 \right\} \quad \ldots \quad (9)$$

$$\text{(IV Epoch), } \frac{v}{V} = e^{\alpha ct} + \alpha(ct - 2a)e^{\alpha(ct-2a)}$$

$$+ e^{\alpha(ct-4a)} \left\{ \alpha(ct - 4a) + \frac{\alpha^2}{\lfloor 2}(ct - 4a)^2 \right\}$$

$$+ e^{\alpha(ct-6a)} \left\{ \alpha(ct - 6a) + \alpha^2(ct - 6a)^2 \right.$$

$$\left. + \frac{\alpha^3}{\lfloor 3}(ct - 6a)^3 \right\} \quad \ldots \quad (10)$$

And so on.

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[1] and [2] Paper No. C, p. 95.

[3] Paper No. A, p. 18. Result (17).

If the striking-point is near the middle of the string, so that $b-a$ is small, then the pulse from the end B overtakes the hammer before it leaves the string, and for an interval defined by $2b<ct<4a$, the pressure[1] can be shown to be

$$F(ct)=2\rho Vc[e^{\alpha ct}+e^{\alpha(ct-2a)}\{1+\alpha(ct-2a)\}$$
$$+e^{\alpha(ct-2b)}\{1+\alpha(ct-2b)\}] \quad \ldots \quad (11).$$

The corresponding velocity of the hammer is given by

$$\frac{v}{V}=e^{\alpha ct}+\alpha(ct-2a)e^{\alpha(ct-2a)}+\alpha(ct-2b)e^{\alpha(ct-2b)} \quad \ldots \quad (12).$$

If b is nearly twice as large as a, so that, as the pulse from the end B having argument $\alpha(ct-2b)$ reaches the hammer, the pulse belonging to the III Epoch relative to the end A, *viz.* the one characterised by the argument $\alpha(ct-4a)$, also arrives there sooner or later, then the pressure is given by

$$F=2\rho Vc[e^{\alpha ct}+e^{\alpha(ct-2a)}\{1+\alpha(ct-2a)\}$$
$$+e^{\alpha(ct-4a)}\{1+2\alpha(ct-4a)+\frac{\alpha^2}{|\underline{2}}(ct-4a)^2$$
$$+e^{\alpha(ct-2b)}\{1+\alpha(ct-2b)\}] \quad \ldots \quad (13).$$

The corresponding velocity of hammer is given by

$$\frac{v}{V}=e^{\alpha ct}+\alpha(ct-2a)e^{\alpha(ct-2a)}$$
$$+e^{\alpha(ct-4a)}\{\alpha(ct-4a)+\frac{\alpha^2}{|\underline{2}}(ct-4a)^2\}$$
$$+\alpha(ct-2b)e^{\alpha(ct-2b)} \quad \ldots \quad (14),$$

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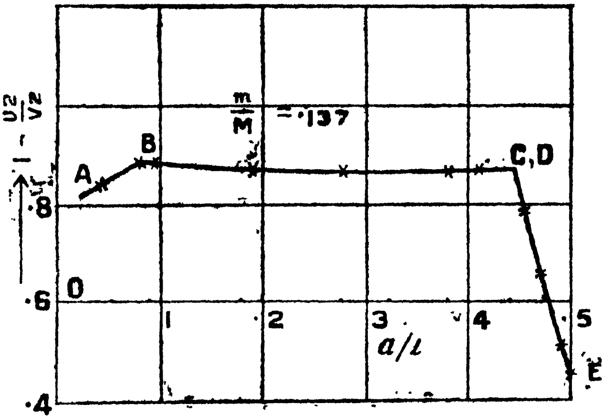
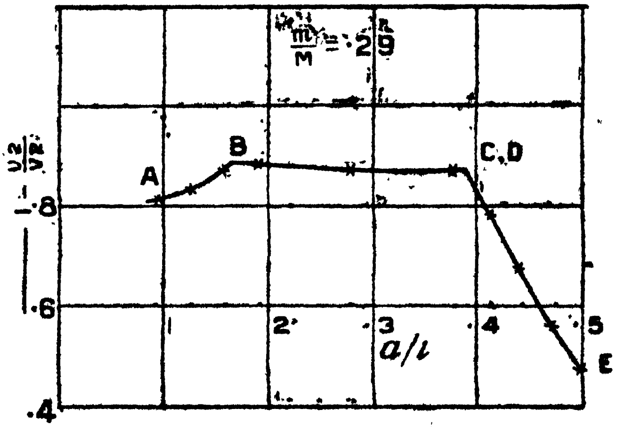
[1] Paper No. B, § 4, p. 317.

Formulae for cases of higher order of complexity will not be required for the numerical calculations undertaken in this paper.



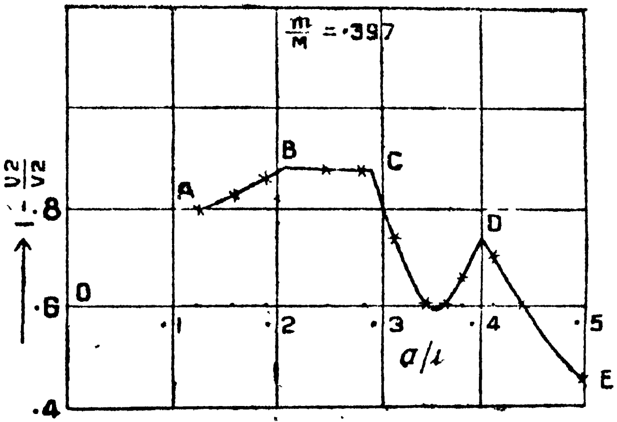
FIG·1

We first calculate the duration of impact with the help of the equations (4), (6) and (7), and substitute this value for t in the expression for v/V, which is found to be a function of a, b and the ratio ρ/m, the value of which has been supplied by George and Beckett. The ratio $(v^2-V^2)/V^2$ of loss of energy to initial energy can thus be calculated and plotted against a/l as George and Beckett have done experimentally. The curve so obtained gives us the Figs. Nos. 1, 2, 3 and 4 corresponding to four different hammers arranged in the order of increasing mass.



FIG·2

The part of the curves marked BC in Figs. 1, 2, 3 is observed to be nearly a straight line. This corresponds to the impact terminating in the II Epoch, the other end B of the string being too remote to affect the motion of the hammer. Calculation for this part was made with the help of (5) and (8). In Fig. 4 there is no such straight part, showing that the impact extends to the III Epoch in the least. The part DE in Figs. 1 to 4 corresponds to the reflection from the end B having overtaken the hammer. The formulas (11) and (12) were used in plotting this part of the curve.



FIG·3

The loop CD is absent in Figs. 1 and 2, and occurs in Figs. 3 and 4 only, *i.e.*, for heavier hammers. The kinematics of this part of the curves is interesting. The hammer after leaving the string is again overtaken by the latter, and a second contact takes place—a fact which has been noted by George and Beckett. The duration of the first contact is obtained by using (5) *i.e.*, the formula for II Epoch, but the value of v/V calculated from this is too small, as was found by comparison with the experimental curve. So the hammer actually departs with a larger final velocity than what it would have acquired, *if the* impact had ceased for good in the II Epoch. This additional momentum is thus gained by a second contact which takes place, when some other pulses arrive, say the one with argument $a\,(ct-2b)$ or $a\,(ct-4a)$, or both. To follow up the motion with rigour involves complicated analysis and has not been attempted here; but an approximate computation can be made. We treat the case as if the hammer does not leave the string at the instant given by (5), but remains attached to the same, until the pulses referred to, arrive, and throw it out. This second contact takes place for a short length DE also. But DE is affected only by the pulse of argument $a\,(ct-2b)$ and not by $a\,(ct-4a)$, whereas CD is affected by both. Thus we use (11) and (12) for DE, and (13) and (14) for CD. The theory for this loop CD not being exact, the agreement between calculated and observed curves is not so good as elsewhere.

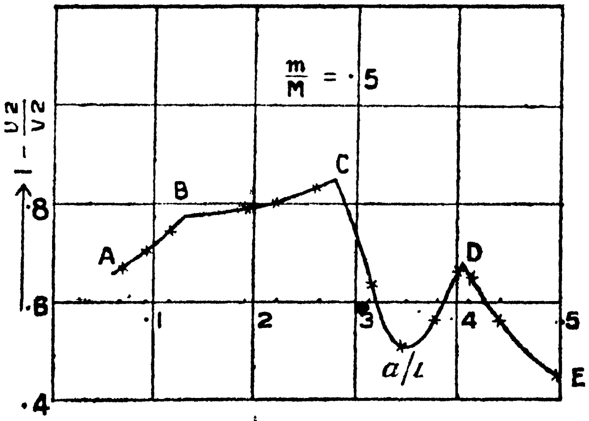


Fig. 4

The part BC of curve in Fig. 4 is not straight but curved, because here the impact extends to III Epoch. The part AB likewise points to the termination of the impact in the IV Epoch. The equations used are (6) and (9) for BC and (7) and (10) for AB in Fig. 4. For smaller values of a/l the calculation is extremely laborious and was not undertaken, though our fomulæ are adequate for the purpose. For heavier hammers than what have been considered here, the duration of impact is very large, and too many reflected pulses complicate the motion giving rise to multiple contacts, which cannot be rigorously discussed with our present formulæ.

I must conclude with my best thanks to Professor C. V. Raman for his guidance and suggestions in the course of this work.

23

Pleochroic Haloes in Cordierite.

BY

C. MAHADEVAN, B.A. (Hons.)

(Plate XVIII)

1. *Introduction.*

Some mineral sections under the polarising microscope reveal pleochroic rings round small nuclei. Originally these were thought to be either of organic origin or due to the storage of helium in the mineral. As is well known, Joly[1] concluded, from the agreement that the radii of these showed with the calculated values of ionisation of the α-particles of the members of uranium and thorium series, that a radioactive nucleus gave out α-rays which brought about concentric haloes in the mineral.

Joly and Fletcher[2] found that while haloes developed in biotite were capable of accurate measurement, those in cordierite showed some discrepancy between calculated and observed values. They observed that the structures are not properly preserved in these haloes; that the margins are diffuse and ill-defined. The greater sensitiveness of cordierite was thought to give rise to more rapid over-exposure and loss of detail. But as a result of the study of several sections of cordierite gneiss from South India, the author finds that the radii of the haloes in the mineral show a close agreement with calculated values and that in many cases the structures are preserved. From the accompanying tables and figures, it is clearly seen how the agreement of the observed with the calculated results shows no more deviation in cordierite than in biotite.

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[1] Joly, Phil. Mag. 13, (1907) p. 381.

[2] Joly and Fletcher, Phil. Mag. 19 (1910) p. 630.

2. *Peculiarities in the halo-structures.*

The haloes in cordierite, just as in biotite, show embryonic rings, 'over-exposed' and 'bleached' haloes. If pleochroic haloes in minerals are due to α-radiations from uranium and thorium series, we should find in them successive rings of the various α-radiating members of the two series. Haloes due to actinium should also be expected if the theory of the genesis[3] of actinium from one of the members of the uranium series is correct. Again, several features such as central bleaching, complete darkening, the occurrence of only the initial rings of a series have all to be accounted for. Joly[4] recognises that it is not hard to show that *prima facie* the structural features are not what one would expect on theoretical grounds. However by assuming that the haloes during their development partake of the properties of latent photographic image and are therefore capable of 'reversal' or 'solarisation' under certain conditions, Joly[5] has found a possible explanation for the observed features. Embryonic rings indicate early stages of development of the halo; the active material has not been sufficient to lithograph all the rings. Haloes of actinium series may be submerged in the effect due to the more preponderating uranium series.[6]

3. *Calculation and measurement of halo radii.*

The haloes, it has been observed, are the impressions made by disintegrating α-rays in the mineral. Bragg and

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[3] Boltwood, Am. Jr. Sc. 25 (1908) p 298.

[4] Joly, Phil. Trans. Roy. Soc. A. Vol. 217 p. 62.

[5] Nature, Vol. 114, p. 160 (1924).

[6] Joly and Fletcher (*loc. cit.*)

Kleeman[7] established that the α-rays, during their rectilinear course ionised the medium through which they passed, and that the loss of the range of α-particles in consequence of their passage through various substances showed a proportion to the square root of the weight of the atom. The loss in the case of a complex molecule was found to be proportional to the sum of the square roots of the weight of the constituent atoms.

The most up to date determination of the range of α-rays in air being Hevesy and Paneth's[8] based mainly on Geiger's[9] work, these values were utilised in deriving the range in the medium. The square root of the mineral was calculated from Krishnan's[10] analyses for this cordierite. (32 SiO_2, 12 Al_2O_3, 15 MgO, 4 H_2O). The density of the mineral was determined as 2·6. Bragg and Kleeman's value for the square root of the atomic weight of air (3·79) was assumed.

From these data, the range in cordierite corresponding to a range of 1 cm. in air (15°C.) was obtained from the well-known formula

$$L=\frac{D}{d}\times\sqrt{\frac{M}{m}},$$

where L = the range in cordierite corresponding to a range of 1 cm. in air (15°C.),

D = density of air (at 15°C.),

d = density of cordierite,

$\sqrt{M}$ = square root of the atomic weight of cordierite,

and $\sqrt{m}$ = square root of the atomic weight of air.

The value of L was found to be 0·005594 mm. This result multiplied by Geiger's values (*loc. cit.*) gave the ranges of the different elements in the mineral.

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[7] Bragg and Kleeman, Phil. Mag. 9 (1905).

[8] Hevesy and Paneth, Radio-activity. Chapter 24. (Oxford, 1926).

[9] Geiger-Zeits Phys. Vol. 8 (1922) p. 54.

[10] Krishnan, Min. Mag. 20, No. 107 (1924).

In Tables I and II calculated ranges in cordierite corresponding to the respective α-ranges in air from uranium and thorium series are given. The ranges are divided into 3 groups, *i.e.*, embryonic, subcoronal and normal.

TABLE I.—Uranium haloes. (Theoretical values).

Stage.	NORMAL.								
	SUB-CORONAL.								
	Embryonic.								
Element.	Ur i	Ur ii	Io	Ra	RaEm.	RaA	RaC	RaC′	RaF
Range in air in cm. at 15°C.	2·830	2·910	3·194	3·389	4·122	4·722	3·800	6·970	3·925
Range in cordierite in mm.	·01583	·01628	·01786	·01895	·02305	·02641	·02125	·03899	·02196

TABLE II.—Thorium haloes. (Theoretical values).

Stage.	NORMAL								
	SUB-CORONAL								
	Embryonic								
Element	Th	RaTh	Thx	ThEm	ThA	ThC	ThC′		
Range in air in cm. at 15°C.	2·720	3·870	4·300	5·000	5·700	4·800	8·600		
Range in cordierite in mm.	·01522	·02165	·02405	·02997	·03188	·02685	·04810		

For the measurement of the haloes a ⅞″ objective and Zeiss micrometer eye-piece gave suitable definition and magnification. The scale of the micrometer eye-piece was calibrated with the help of a ruled grating having 500 lines to the centimetre and thence the dimensions of the haloes could be directly read from the eye-piece scale. In the case of large and irregular nucleus or rectangular nucleus, the halo is seen to be subcircular. Erroneous readings are apt to be made if great care is not bestowed on their measurement. Joly and Fletcher (*loc. cit.*) recognising the possibility of error from this source, suggested the deduction of the mean nuclear diameter from the diameter of the halo. When this method is followed, there is little chance of the measurements going wrong even in the case of subcircular or oval haloes. Often the zircon nucleus is darkened; in such a case, the boundary of the nucleus was determined by viewing the section in the reflected light. It is found necessary to carefully distinguish between a darkened ring round a nucleus and a dark nucleus itself.

4. *Uranium haloes.*

The stages of development of the uranium haloes have been discussed at length by Joly.[11] Embryonic, subcoronal and normal stages are the three main divisions into which the haloes of uranium series can be roughly classified. In the first case we have the limit ring of 0.023 mm. in cordierite corresponding to a range of 4.122 cms. in air for RaEm. Within this range may be found rings due to uranium, radium and ionium. The next stage indicates a range of 0.0264 mm. in cordierite, corresponding to a range of 4.722 cm. in air, due to RaA. The coronal stage is limited by a halo of 0.039 mm. radius in cordierite, corresponding to the 6·97 cms. range in air, due to RaC′. The occurrence of embryonic haloes, of the obliteration of inner rings and of cases of reversal have all been accounted for by Joly and the points need not be repeated here.

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[11] Joly. Phil. Trans. Roy. Soc. (*loc. cit.*)

TABLE III.—Uranium haloes (normal).

Stage.	NORMAL.					
	Sub-Coronal.					
	Embryonic.					
Element. / Nucleus.	Ur	Io	RaEm	RaA	RaC'	
Irregular ...		·018		·026	·039	Sub-coronal ring pink, outer-most yellow.
Circular ...	indistinct			bleached	·038	Inner ring ill-defined, middle ring bleached.
Nearly circular ...	·016			·026	·038	
Nearly circular ...	·016		·023			Two embryonic rings clearly seen.
Very irregular ...	Indistinct			·027	·039	Inner features nearly obliterated.
Very irregular ...	Indistinct			·027	·039	
Border darkened	·016			·027		Outer ring deeply yellow
Circular ...		·018				A single yellow ring round a circular nucleus. Embryonic.
Clear circular ...	·016					Structureless, pale yellow
Circular ...	Bleached				·038	A deeply yellow ring bleached inside.
Oval ...	Bleached			·027	·038	Two rings distinct.
Circular ...		·018	·023			Two yellow distinct rings Embryonic.
Irregular ...		·017				A single clear ring.
		·017		·026		

5. *Emanation haloes* (*Uranium*).

In a properly preserved halo, the embryonic stages should show rings due to Ur, Io, Ra, RaEm, but there are haloes in which the first ring gives measurement for RaEm. The subsequent structures may be developed but no trace of the earlier members are seen. Such haloes have been called by Joly "emanation haloes." To account for these haloes, Joly assumed that the radon got occluded in the nucleus and began its further disintegration round this nucleus. Some readings from the author's observations are set forth in Table IV.

Iimori and Yoshimura[12] suggest that the emanation halo and the subsequent rings may be ascribed to some other group of elements which resemble closely the post-emanation members of the uranium series in their α-range. This view seems far-fetched, especially in view of the fact that no such series showing close agreement with post-emanation members of the uranium family in its α-range, has been established to exist.

TABLE IV.—Uranium emanation haloes.

Element / Nucleus	RaEm	RaA	Ra C′	Remarks
......	·023	...	·038	Rings not quite distinct: outer ring yellow.
Irregular, rounded	·024	...	·039	Inner ring distinct and dark, outer faint, but defined.
Irregular ...	·024	...	·039	Two clear rings, outer dark yellow.
Rectangular ...	·023	...	·039	Rings quite sharp and clear.
Irregular ...	...	·027	·039	First ring masked in the sub-coronal darkening.
Triangular ...	·023	...	·039	Two clear rings.
......	...	·027	·039	One side merged in garnet.

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[12] Iimori and Yoshimura: Scientific papers of the Inst. Phys. Chem. Research, Vol. 5, No. 66 (1926).

6. *Thorium haloes.*

Embryonic, sub-coronal and normal haloes due to thorium series have been found in the sections examined. The development of the thorium haloes is analogous to that of uranium. The same classification in the stages of development is set forth here as in the case of the uranium series.

TABLE.—V Thorium haloes.

Stage	NORMAL					
	SUB-CORONAL					
	Embryonic					
Element / Nucleus	Th	RaTh	Th X and Th Em	Th A	Th C′	
Oval zircon ...	...	·021	...	...	·048	One side absorbed by magnetite.
Oval ...	...	...	·030	...	·048	One side corroded.
Small, dark edge	·015	...	·029	...	...	Embryonic rings.
Circular ...	·015	·021	...	...	...	,,
Dark ...	·015	Bleached		...	·048	Intermediate rings bleached.
......	...	·021	Bleached		·048	......
Clear minute ...	·015	...	...	...	...	A single structureless ring.
Irregular ...	...	·021	...	...	·049	Outer darker ring masks sub-coronal stage.
Circular ...	·015	...	·029	...	...	Outer ring yellow.

TABLE V.—Thorium haloes.—*contd.*

Stage	NORMAL					
	SUB-CORONAL					
	Embryonic					
Oval ...	...	·021	·030	...	...	Inner ring darkish, outer faint.
,, ...	Indistinct		...	·031	·048	......
Dark boundary ...	...	...	...	·031	·048	Inner ring darkened.
Nearly circular ...	Indistinct		Bleached		·048	Sub-coronal stage clearly bleached.
......	...	...	...	...	·048	......
Oval ...	·015	...	·026	...	·049	Second ring bleached.

7. *Dwarf haloes.*

Joly[13] noted the occurrence of minute rings (radius between 0·005 mm. and 0·011 mm. in biotite) round small nuclei. These readings could not be found to correspond with haloes due to any known range of α-particle. He thought that these represented the activity of a hitherto undiscovered element and called it 'Hibernium.'[14] Rosseland[15] in a letter to Joly published in 'Nature,' thought that from physical considerations, the suspected new element might be merely yttrium. In Table VI are given the radii of these 'dwarfs' in biotite and cordierite from which corresponding ranges in air are indicated.

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[13] Joly, Nature 109, p. 517.

[14] Joly, Nature 109, p. 578.

[15] Nature, 109, p. 711.

Table VI.—Dwarf haloes (calculated ranges in air).

Range in biotite mm.	Range in cordierite mm.	Range in air cm.
·0059	·0067	1·2
·0100	·0117	2·1
·0665	·0078	1·4
·0114	·0134	2·4

Table VII.—Dwarf haloes (Observed).

Nucleus	γ_1	γ_2	γ_3	Remarks.
Small oval nucleus	·007	·012		Two rings quite distinct.
Rectangular	·007	·011		Inner ring dark, outer, faint yellow.
Perfectly circular	·008		·021	Inner ring clear.
Circular	·007		·020	Darkish inner ring and faint outer ring.
Dark nucleus	·007		·021	Rings distinct.
Much darkened	·007			Clear yellow ring round dark nucleus.
		·012		A faint ring.
Nearly circular		·011		Darkening round nucleus.
	·008	·012		Outer ring well-defined.
Circular		·010		Minute dark distinct ring.
Circular	·008	·012		Outer ring faint.
		·010	·021	

In the "dwarf" haloes, very often, a ring of 0·021 mm. radius in cordierite appears along with the smaller rings.

Iimori and Yoshimura (*loc. cit.*) found these dwarf rings and concluded that these 'dwarfs,' their own 'Z' haloes and Joly's[16] emanation and 'X' haloes all belong to the actinium series. In view of the several conditions that have to be postulated for the assumption and in the absence of more conclusive evidence on the point, it is doubtful if such a suggestion can find support.

Further work is being carried on in this problem and it is expected that some satisfactory solution would be forthcoming for the doubtful points.

8. *Summary and Conclusions.*

(1) Pleochroic haloes occurring in cordierite from South India were studied under the polarising microscope.

(2) Embryonic rings, normal, "emanation," "over-exposed" "bleached" and "dwarf" haloes were met with in the sections examined.

(3) It is found that contrary to the observations of Joly and Fletcher, the radii of these haloes show close agreement with the calculated values for the α-range of the members of the uranium and thorium series in the mineral. In many cases, the successive rings are well-preserved.

(4) It is shown that there is no more discrepancy between the expected and observed results in the haloes of cordierite than in those of biotite.

The work was carried out in the laboratories of the Indian Association for the Cultivation of Science. The author's grateful thanks are due to Prof. C. V. Raman, F.R.S., for suggesting this problem and for his inspiring guidance and valuable criticism during its progress.

• Nature, Vol. 114. p. 160.

Description of figures (Plate XVIII).

Fig. 1—A uranium and a thorium halo.
Fig. 2—A group of centre-bleached haloes.
Fig. 3—A centre-bleached thorium halo—large nucleus (highly magnified).
Fig. 4—Irregular nucleus and faint outer ring.
Fig. 5—Uranium emanation halo.
Fig. 6—Uranium emanation halo (highly magnified).

PLEOCHROIC HALOES IN CORDIERITE.

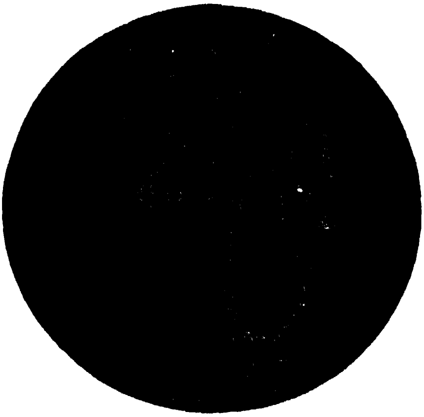

Fig. 1

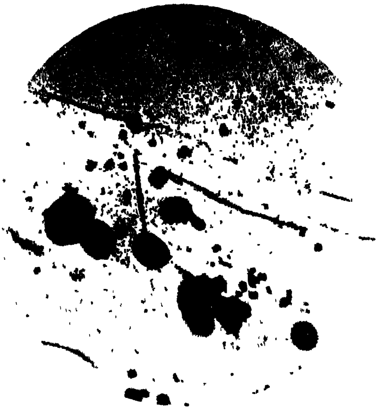

Fig. 2

Fig. 3

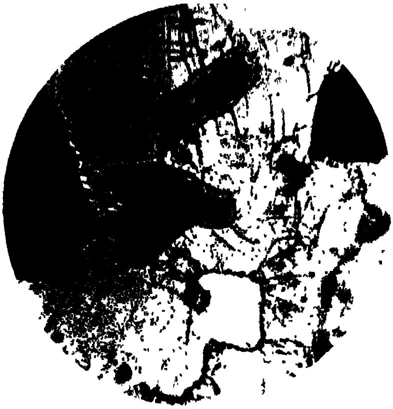

Fig. 4

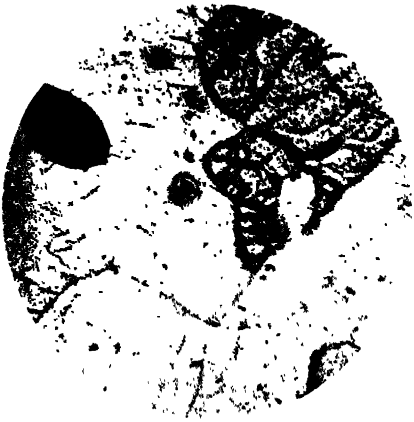

Fig. 5

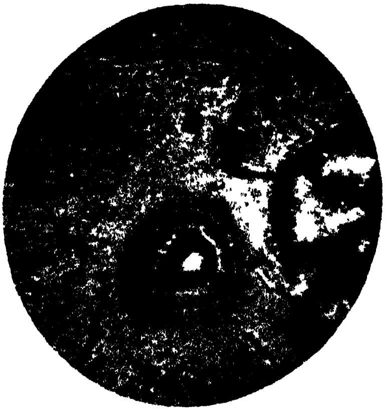

Fig 6